Notes

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Tin(II) and Dimethyltin(IV) Derivatives of Amino Acids

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The extraordinary activity of the organotin biocides is crucially dependent upon the effectiveness of their interaction at an active site which presumably involves coordination to an amino acid.[2] The first amino acid esters of tin of the type R_3SnAA were reported in 1965 as a protecting group for the carboxylate function,[3] and we have prepared series of trimethyl- and tricyclohexyltin amino acids and dipeptides for spectroscopic study by the azeotropic distillation of water from benzene solutions of the corresponding stannol or bis(trialkyltin) oxide and the acids.[4,5] It could be shown that when the alkyl groups about tin were not too bulky, intermolecular coordination through the amino group occurred to give trigonal-bipyramidal geometry at tin in a one-dimensional, associated structure.[6] This is unusual since tin has a known preference for oxygen, and bridging by the carbonyl group would have been expected.[7]

This study extends the tin–amino acid derivative series to tin(II) and dimethyltin(IV). We report the synthesis and characterization of diglycinatotin(II), dimethytin(IV) diglycinate, and dimethyltin(IV) di-β-alaninate.

Experimental Section

Infrared spectra were recorded as Nujol mulls on a Beckman IR-12 spectrometer. Tin-119m Mössbauer spectra were recorded at 77 K and fit by published procedures.[8] The x-ray powder patterns of compounds held in nitrogen-filled Lindemann glass capillary tubes were recorded on Diano x-ray diffraction equipment using a Co Kα source at 35 kV in a 100-mm diameter camera.

Diglycinatotin(II). Anhydrous tin(II) chloride (3.8 g; 0.02 mol) and glycine (3.0 g; 0.04 mol) were slurried together under nitrogen with methanol dried over magnesium filings. Triethylamine (5.6 mL; 0.04 mol) dried over barium oxide was added dropwise with stirring to form a thick, white precipitate immediately. The mixture was allowed to reflux overnight and the precipitate collected by filtration under nitrogen, washed thoroughly with dry methanol, and dried in vacuo. The product, obtained in 75–80% yield, decomposed at temperatures >210 °C and, on attempted sublimation, was air stable and insoluble in all common organic solvents. Anal. Calcd for $C_4H_8O_4N_2Sn$: C, 18.01; H, 3.02; Sn, 44.48. Found: C, 18.42; H, 3.24; Sn, 43.60.

Other amino acids in our hands failed to yield a product by this procedure.

Dimethyltin(IV) Diglycinate. Dimethyltin(IV) oxide (2.47 g; 0.015 mol) and glycine (2.26 g; 0.03 mol) were allowed to reflux in toluene (100 mL) under nitrogen with dimethylformamide (50 mL) as a catalyst until the expected amount of water (ca. 0.3 mL) had distilled azeotropically into a Dean-Stark trap. The product precipitated in 70–80% yield as a white solid and was filtered under nitrogen, washed with petroleum ether, and dried in vacuo. The product, which was insoluble in all common organic solvents, readily hydrolyzed in air and decomposed above 200 °C and on attempted sublimation. Anal. Calcd for $C_6H_{14}O_4N_2Sn$: Sn, 39.98. Found: Sn, 39.62.

Dimethyltin(IV) Di-β-alaninate. This was prepared analogously to give a white solid in 80% yield which was insoluble in all common organic solvents, was readily hydrolyzed by atmospheric moisture, and decomposed above 200 °C. Anal. Calcd for $C_8H_{18}O_4N_2Sn$: Sn, 36.53. Found: Sn, 36.82.

Other amino acids in our hands yielded intractable oils by this procedure.

Results and Discussion

Tin(II). Few tin(II) x-ray structures are known for compounds containing organic ligands,[7,9] and hence most structural conclusions are inferred from the data from physical methods. Divalent tin compounds generally achieve higher coordination as in tin(II) sulfate[10] or the triformato-[11] or trichlorostannate[12] anions which contain pyramidal, three-coordinated tin(II), and recent structural investigations of tin(II)–oxygen compounds show that the coordination numbers at tin(II) can rise above 3. Indeed, coordination numbers of 4 are found in $Sn(S_2COCH_3)_2$, $Sn[S_2CN(C_2H_5)_2]_2$,[13] and $Sn(C_6H_5COCHCOCH_3)_2$[14] and of 6 are found in $Sn_2EDTA\cdot 2H_2O$[15] and $Sn^{II}Sn^{IV}(O_2CC_6H_4NO_2\text{-}o)_4O\cdot THF$[16] which are, respectively, five- and seven-coordinated when the stereochemically active lone pair is included. The amino acid glycine is a potentially polydentate ligand toward tin(II).

Infrared data can distinguish free from coordinated NH_2 groups in metal complexes of amino acids.[4,5] Coordinated amino groups show a lowering of the N–H stretching frequencies accompanied by an enhancement of their intensities. Infrared data for the amino acid derivatives and related compounds are listed in Table I. Comparison with $\nu(NH_2)$ in matrix-isolated glycine[17] and sodium glycinate, both of which contain free NH_2 groups (the latter in an anion), shows that there has been substantial lowering of frequency in the tin(II) derivative which resembles more closely the zwitterionic form of glycine in which there are NH_3^+ groups and trimethyltin(IV) glycinate which is known to be bridged through coordinated amino groups.[6] Since there is no evidence of higher frequency absorptions, we can conclude that both amino groups are coordinated.

Infrared $\nu(O{-}C{=}O)$ stretching frequencies can also be used to distinguish coordinated from free carbonyl groups, but care must be taken to identify the bending absorption of the amino group which lies in the same region. Coordination and an increase in the ionic character of the carboxylate bonds both tend to lower the asymmetric $\nu(O{-}C{=}O)$ absorption. Trimethylsilyl acetate possesses a normal ester structure in which the carbonyl stretching frequency occurs at 1725 cm^{-1}. The corresponding absorption at 1576 cm^{-1} in trimethyltin(IV) acetate[18] is typical of the associated tin(IV) carboxylates.[19] The $\nu_{asym}(O{-}C{=}O)$ is found at 1635 cm^{-1} in trimethyltin(IV) alaninate which does not contain coordinated carboxyl groups and at 1600 cm^{-1} in tricyclohexyltin(IV) alaninate which does.[4,5] The asymmetric $\nu(O{-}C{=}O)$ stretch is assigned at 1644 cm^{-1}, in the range of uncoordinated carbonyl groups. Since there is no evidence of lower frequency absorptions, we conclude that neither carboxyl group is coordinated.

The ^{119m}Sn Mössbauer data are listed in Table II. The high isomer shift (IS) value confirms the presence of tin as tin(II).[20] The compound exhibits an easily observable spectrum at ambient temperatures, from which, together with the similar finding for the trimethyltin(IV) derivative whose solid-state structure was shown to consist of an amino-bridged, associated, one-dimensional polymer,[6] we conclude that tin(II) glycinate is polymeric in at least one dimension.[21] X-ray powder diffraction data show that the tin(II) and trimethyltin(IV) glycinates are not isomorphous.

Given that in tin(II) glycinate both amino groups are coordinated and both carbonyl groups are free, three possible structures must be considered: (a) a one-dimensional polymer based upon a square pyramidal geometry at tin with one inter-

Table I. Infrared Stretching Frequencies of the Amino, Carboxylate, and Methyltin Groups in Tin-Containing Amino Acid Derivatives (cm^{-1})

	$Sn(gly)_2$	Hgly[a]	Na(gly)[b]	$(CH_3)_3$-Sn(gly)[b]	$(CH_3)_3$-Sn(ala)[b]	$(CH_3)_2$-$Sn(gly)_2$	$(CH_3)_2$-$Sn(ala)_2$
$\nu(NH_2)$	3294 3169 3100	3170	3380	3311 3244 3224 3199 3154	3310 3240 3150	3252 3160 3122	3265 3218 3121
$\nu_{asym}(O-C=O)$	1644	1605	1600	1630	1636	1629	1629
$\nu_{asym}(Sn-C)$				545	541	522	566
$\nu_{sym}(Sn-C)$				507	510		

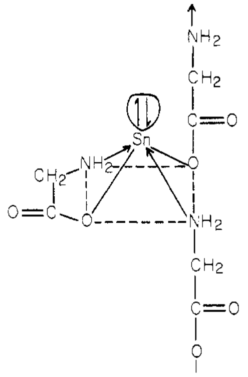
[a] Reference 17. [b] Reference 5.

Table II. ^{119m}Sn Mössbauer Data for Tin-Containing Amino Acid Derivatives at 77 K[a]

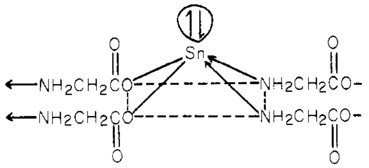
Compd	IS ± 0.06, mm/s	QS ± 0.12, mm/s	Γ_1	Γ_2
$Sn(gly)_2$	3.06	1.88	0.92	1.04
$(CH_3)_2Sn(gly)_2$	1.14	3.73	1.50	1.71
$(CH_3)_2Sn(\beta\text{-ala})$	1.28	3.77	1.30	1.36
$(CH_3)_3Sn(gly)$[b]	1.26	3.14	1.16	1.07
$(CH_3)_3Sn(\beta\text{-ala})$[b]	1.30	3.08	1.20	1.14

[a] All compounds listed showed a spectrum at ambient temperatures. [b] Reference 5.

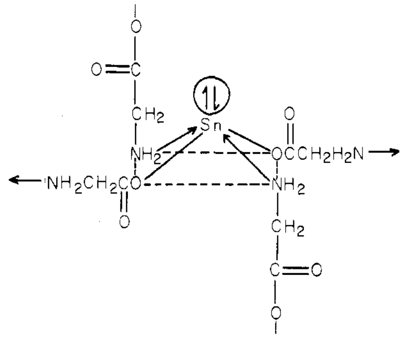
and one intramolecularly coordinated amino group



(b) a one-dimensional polymer based upon a square-pyramidal geometry at tin with two bridging amino groups attached cis to the tin to give a two-stranded chain



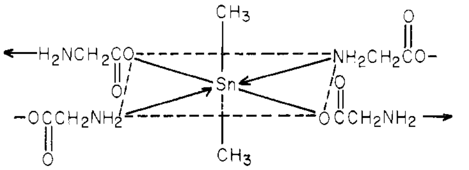
and (c) a two-dimensional polymer based upon a square-pyramidal geometry at tin in which both amino groups bridge intermolecularly to different adjacent tin atoms in a cis or trans configuration



The last-named structure (c) would be expected to result in the most tightly bound lattice and is thus favored.

In D-penicillaminolead(II) the amino acid acts as a tridentate chelating ligand with respect to the lead atom which binds both the amino and carboxyl groups.[22]

Tin(IV). Examination of the lowered infrared stretching frequencies of the $\nu(NH_2)$ and the normal frequencies of the $\nu(O—C{=}O)$ absorptions and use of the criteria previously discussed lead to the conclusion that both amino groups are coordinated and both carbonyl groups are free in trimethyltin(IV) glycinate and alaninate. This specifies six-coordination at tin. The absence of the symmetrical $\nu(SnC_2)$ absorption indicates that the methyl groups must be in a trans configuration. The large Mössbauer quadrupole splitting (QS) values are corroboratory since point-charge calculations predict the magnitude of the QS to be twice that of the cis O_h isomer,[23] and the value for dimethyltin(IV) species is generally near 4 mm/s.[20] The ratio ρ = QS/IS is 3.0–3.3, again indicative of higher coordination at the tin atom.[20] Finally, both compounds, like their trimethyltin(IV) analogues, exhibit a strong ambient-temperature spectrum, and we infer an associated structure in one or more dimensions. We cannot distinguish on the basis of the evidence available between a trans,cis,cis or the trans,trans,trans structure



While this note was being processed for publication, a communication appeared describing diorganotin(IV) derivatives of glycylglycine, the dimethyltin compound synthesized from the dichloride and the peptide in sodium methoxide/methanol, and proposing a trigonal-bipyramidal geometry at tin with equatorial organic groups on the basis of 77 K Mössbauer data alone.[24]

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Registry No. $Sn(gly)_2$, 61618-08-4; $(CH_3)_2Sn(gly)_2$, 61618-10-8; $(CH_3)_2Sn(\beta\text{-ala})_2$, 61618-12-0; dimethyltin(IV) oxide, 2273-45-2; ^{119}Sn, 14314-35-3.

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Potentiometric and Polarimetric Studies of Complexation of Molybdenum(VI) and Tungsten(VI) by Aspartic Acid and Glutamic Acid

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Despite the extensive literature on the coordination chemistry of molybdenum(VI) and tungsten(VI), few formation constants have been reported for their complexes.[1] This situation is no doubt due to the competitive formation of isopolymolybdate and isopolytungstate species in acidic solution.[2-4] In basic solution, little or no complex forms due to the exceedingly high stability of the MoO_4^{2-} and WO_4^{2-} species.

Recently, Singh and Srivastava reported stepwise formation constants for 1:1, 1:2, and 1:3 aspartic acid and glutamic acid complexes of Mo(VI), W(VI), and V(IV).[5] The formation constants were computed from potentiometric titration data by the methods of Irving and Rossotti.[6] Since Mo(VI) and W(VI) complexes generally contain either an MO_2 or an MO_3 core with the coordination sphere of the metal completed by coordination to four or three donor atoms, respectively, it seems unlikely that complexes of 1:2 and 1:3 stoichiometry exist in aqueous solution. To determine the extent to which Mo(VI) and W(VI) are complexed by aspartic acid and glutamic acid in aqueous solution, we have studied these systems by potentiometry and polarimetry. A major objective of this communication is to describe how formation constants of Mo(VI) complexes can be correctly determined by the potentiometric titration method.

Table I. Optical Rotation (α) of Aspartic Acid as a Function of Solution Composition

pH	α	pH	α
0.050 M Aspartic Acid, 0.200 M KNO_3			
9.32	−0.171	5.07	−0.232
7.05	−0.249	3.27	0.088
5.90	−0.250		
0.050 M Aspartic Acid, 0.050 M Na_2MoO_4, 0.200 M KNO_3			
9.27	−0.142	5.12	0.661
7.37	−0.178	4.01	0.314
6.17	0.335	3.01	0.233
0.05 M Aspartic Acid, 0.050 M Na_2WO_4, 0.200 M KNO_3			
9.29	−0.147	5.00	−0.208
7.60	−0.198	4.12	−0.014
6.24	−0.198	2.19	−0.002

Table II. Continuous Variation Data for the Mo(VI)-Aspartic Acid System[a, b]

Mol fraction Mo(VI)	α(Mo + Asp)[c]	Δα[d]
0.00	−0.251	0.000
0.10	−0.043	0.183
0.20	0.131	0.332
0.30	0.213	0.389
0.40	0.280	0.431
0.50	0.286	0.412
0.60	0.254	0.354
0.70	0.210	0.285
0.80	0.141	0.191
0.90	0.080	0.105
1.00	0.000	0.000

[a] 25 °C; pH 6.19; ionic strength controlled with 0.20 M KNO_3. [b] [Mo(VI)] + [aspartic acid] = 0.050 M. [c] Optical rotation. [d] Δα = α(Mo + Asp) − α(Asp), where α(Asp) is the optical rotation of aspartic acid at the same concentration as in the Mo-aspartic acid solution.

Experimental Section

Analytical reagent grade $Na_2MoO_4\cdot 2H_2O$ and $Na_2WO_4\cdot 2H_2O$ were used as received. L-Aspartic acid and L-glutamic acid were obtained from Eastman Organic Chemicals and were used as received.

pH measurements were made at 25 ± 1 °C with an Orion 701 pH meter, which was calibrated with Fisher Certified standard solutions of pH 4.00, 7.00, and 10.00. Polarimetric measurements were made at 25 °C with a Perkin-Elmer Model 141 polarimeter using the 365-nm line of the mercury source. A water-jacketed cell of 100-mm length and 5-mL total volume was used. The precision of the measurements is estimated to be ±0.002 degrees of arc.

Results and Discussion

Assuming that the optical activity of aspartic acid will change upon complexation, polarimetric measurements were made to determine if Mo(VI) and W(VI) are complexed by aspartic acid. The results are given in Table I. In the presence of Mo(VI), the optical rotation is nearly the same as that of the free aspartic acid at pH 9.27. The small difference could be due to the formation of a sodium-aspartic acid complex. As the pH is decreased below pH 7, the optical rotation of the Mo-aspartic acid solution becomes increasingly different from that of aspartic acid, indicating complexation by Mo(VI). The difference reaches a maximum between pH 5 and 6 and then decreases as the pH is decreased below 5, indicating that the largest amount of complex forms in the pH range 5-6. At higher pH, the complex dissociates due to the competitive formation of MoO_4^{2-}, while at low pH isopolymolybdates form. In contrast, the optical rotation data for the W(VI)-aspartic acid solution shows only small differences from that for the aspartic acid solution, indicating little if any complexation of aspartic acid by W(VI).

The stoichiometry of the Mo(VI) complex at pH 6 was determined by the method of continuous variations. The results given in Table II indicate the stoichiometry to be 1:1.