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Syntheses and Characterization of Pentacoordinate Organo-Tin(IV) Complexes

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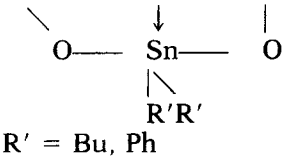
ABSTRACT

Ten novel pentacoordinate organo-tin complexes were prepared and characterized. Single crystal structure determinations by X-ray diffraction and also chemical investigations were made.

Crowe and his group have reported on the chemotherapeutic properties of tin compounds, including antitumor activity [1,2]. Since then, a wide interest has developed in this field. We have previously prepared a variety of pentacoordinate tin complexes in which the metal is coordinated with tridentate ligands containing nitrogen and oxygen [3,4]. In line with these developments, we now report the synthesis of pentacoordinate organotion complexes with salicylaldehyde Schiff bases of amino acids:

o-$OHC_6H_4CHO + NH_2CH(R)COOK \rightarrow$
o-$OHC_6H_4CH{=}NCH(R)COOK$
R = H, $(CH_3)_2CHCH_2-$, $PhCH_2-$, $CH_3SCH_2CH_2-$
o-$OHC_6H_4CH{=}NCH(R)COOK + R_2'SnCl_2 \rightarrow$



R′ = Bu, Ph

Ten novel pentacoordinate organotin complexes, which may be designated as "bicycloazastannoxides," have thus been prepared. They have a yellow color, and their physical and spectroscopic data are shown in Tables 1–3

When we started out with optically active amino acids, the Schiff bases obtained and the coordinated tin complexes are also optically active, as shown in Tables 4 and 5.

Under electron bombardment, the fragmentation of bicycloazastannoxides can be divided into two categories: (1) the dibutyltin complexes which undergo cleavage of butyl groups but exhibit formation of molecular cations [M^+] and (2) the diphenyltin complexes which retain their phenyl groups but cast off CO_2 from the ligand. The mass spectra of the two types of compounds are as follows:

Complex 1—the dibutylbicycloazastannoxide: 412 (M^+, 5%), 367 (16%), 298 (26%), 254 (M^+-2Bu-CO_2, 100%), 225 (38%), 120 (10%), 91 (28%).

Complex 7—the diphenylbicycloazastannoxide: 421 (M^+, CO_2, 100%), 344 (26%), 303 (68%), 197 (93%), 167 (52%), 120 (91%), 77 (34%).

EXPERIMENTAL

Melting points were determined on a PHMK melting point stage without correction. Elemental analyses were carried out on a CHN corder M73 apparatus. The ^1H NMR spectra were taken on a JNMPMX 60MH NMR spectrometer and IR spectra on the Nicolet FT-IR 50X spectrometer, using a KBr disc, MS on the VG 7070E ΠHF mass spectrometer with EB at 70 ev intensity.

1. Syntheses of dibutyl or diphenyl tin dichlorides were carried out according to literature reported methods [5].
2. Syntheses of Schiff bases of amino acids: Two millimole of solid amino acid was dissolved

Dedicated to Prof. Yao-Zeng Huang on the occasion of his eightieth birthday.

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TABLE 1 The Elemental Analysis, Yields, and Melting Points of Bicycloazastannoxides

Entry	R	R^1	MW	mp (°C)	Yields (%)	C	H	N
1	H	Bu	410	123.5	80	49.84 (49.78)	6.23 (6.14)	3.37 (3.42)
2	Me	Bu	423.7	98.1	83	50.94 (50.98)	6.45 (6.42)	3.23 (3.30)
3	*i*Bu	Bu	466	92.4	60	54.04 (54.10)	7.13 (7.13)	2.93 (3.00)
4	$PhCH_2$	Bu	499.7	116.8	85	57.60 (57.63)	6.23 (6.29)	2.85 (1.80)
5	$MeS(CH_2)_2$	Bu	483	78.8	64	49.72 (49.61)	6.50 (6.45)	2.82 (2.89)
6	H	Ph	449.7	183.5	78	56.10 (56.44)	3.69 (3.80)	3.13 (3.11)
7	Me	Ph	463.7	198–200	70	56.53 (56.94)	4.17 (4.80)	3.05 (3.02)
8	*i*Bu	Ph	506	198	67	59.57 (59.34)	5.00 (4.98)	2.75 (2.77)
9	$PhCH_2$	Ph	540.7	192–194	75	62.26 (62.21)	4.20 (4.19)	2.95 (2.91)
10	$MeS(CH_2)_2$	Ph	524	115–117	87	55.03 (54.99)	4.44 (4.42)	2.57 (2.67)

TABLE 2 IR Spectra of Bicycloazastannoxides

Entry	μC=O	μC=N	μph–O	μSn–O	μSn–N
1	1630 (s)	1859 (s)	1302 (m)	531 (m)	440 (m)
2	1622 (s)	1581 (s)	1302 (m)	547 (m)	440 (m)
3	1617 (s)	1614 (s)	1302 (m)	520 (m)	440 (m)
4	1614 (s)	1589 (s)	1302 (m)	547 (m)	450 (m)
5	1687 (s)	1614 (s)	1302 (m)	547 (m)	440 (m)
6	1687 (s)	1614 (s)	1310 (m)	547 (m)	480 (m)
7	1687 (s)	1614 (s)	1310 (m)	547 (m)	448 (m)
8	1679 (s)	1622 (s)	1318 (m)	564 (m)	480 (m)
9	1632 (s)	1622 (s)	1291 (m)	547 (m)	436 (m)
10	1679 (s)	1614 (s)	1310 (m)	547 (m)	432 (m)

in 1% KOH-alcoholic solution, with slight warming to ensure the complete dissolution of the amino acid. The solution was cooled to −10°, then 7 mmol of salicyladehyde was added to the solution which turned yellow. After the reaction had been completed, excess anhydrous ether was added to cause precipitation of the Schiff base of the amino acid. The product was recrystallized from an alcohol-ether solution. Yields obtained varied from 65 to 83%.

3. Preparation of the bicycloazastannoxides: A typical procedure is as follows: Into 20 mL of dry benzene, a mixture of 2 mmol (0.23 mL) of Et_3N and 1.5 mmole of the Schiff base and 1.5 mmol of R_2SnCl_2 dissolved in 20 mL of benzene was dropped in within an hour. Stirring was continued for another 2–3 hours. Any precipitate that had formed was filtered off, and the yellow filtrate containing the product was concentrated in a rotary evaporator to 5 mL. Five milliliters of ligroin (bp 60–90°) was added to aid in the precipitation of the product which was collected and recrystallized from CH_2Cl_2-ligroin solution.
4. Determination of the structure of a single

TABLE 3 H NMR Spectra of Bicycloazastannoxides

Entry	C_6H_4	=CH	–CH(R)	R 2R′
1	6.8–7.50 (m, 4H)	8.43 (s, 1H)	4.40 (s, 2H)	R′=Bu 0.96–1.67 (m, 18H)
2	6.7–7.30 (m, 4H)	8.33 (s, 1H)	4.16 (s, 1H)	R=Me, R′=Bu 0.80–1.67 (m, 21H)
3	6.8–7.30 (m, 4H)	8.26 (s, 1H)	4.10 (s, 1H)	R=i-Bu, R′=Bu 0.81–1.70 (m, 27H)
4	6.8–7.30 (m, 4H)	8.30 (s, 1H)	4.20 (s, 1H) R=$PhCH_2$:	R′=Bu 0.90–1.56 (m, 18H) Ph:6.38–7.50 (m, 5H), CH_2:3.30 (s, 2H)
5	6.71–7.50 (m, 4H)	8.46 (s, 1H)	4.30 (s, 1H)	R′=Bu 0.80–2.80 (m, 18H) R=$MeSCH_2CH_2$:0.80–2.80 (m, 7H)
6	7.00–8.00 (m, 4H)	8.46 (s, 1H)	R=H:4.35 (s, 2H)	R′=Ph:7.00–8.00 (m, 10H)
7	7.00–8.00 (m, 4H)	8.33 (s, 1H)	4.20 (s, 1H)	R=Me:1.50–1.80 (d, 3H) R′=Ph:7.00–8.00 (m, 10H)
8	7.00–8.00 (m, 1H)	8.30 (s, 1H)	4.20 (s, 1H)	R=iBu:1.50–1.80 (m, 9H) R′=Ph:7.00–8.00 (m, 10H)
9	6.70–8.00 (m, 4H)	8.50 (s, 1H)	4.30 (s, 1H)	R′=Ph, 6.70–8.00 (m, 10H) R=$PhCH_2$:6.70 (m, 5H), 3.30 (d, 2H)
10	6.66–8.10 (m, 4H)	8.50 (s, 1H)	4.33 (s, 1H)	R′=Ph:6.66–8.10 (m, 10H) R=$MeSCH_2CH_2$:1.99–2.60 (,7H)

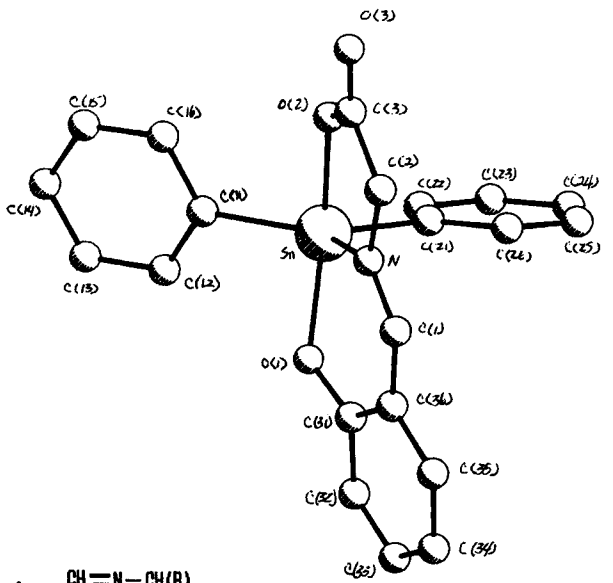
TABLE 4 Optical Activities of Schiff Base, o-$HOC_6H_4CN{=}NCHR\text{-}COOK$

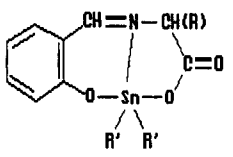
Entry	R	Color	MW	mp (°C)	$[\alpha]_D^{20}$
1	Me	yellow	231.3	154–155	+74 (c=1, MeOH)
2	Me_2CHCH_2	yellow	273.4	171–173	−15 (c=0.3, MeOH)
3	$PhCH_2$	yellow	307.4	166–167	−316 (c=0.5, MeOH)
4	$MeS(CH_2)_2$	yellow	291.4	167–168	−42 (c=0.33, MeOH)

crystal of compound **6**: The bicycloazastannoxide **6** (Tables 2 and 3) was incubated in CH_2Cl_2-ligroin (2:1) to give a single crystal of dimensions 0.2 × 0.2 × 0.3 mm, which was mounted on an ENRAF-NONIUS CAD4 diffractometer and examined by Mo-K_α irradiation (0.71073 Å). Independent reflection data were collected in the range of $2° \leq \theta \leq 25°$, with -2θ scan mode at room temperature.

TABLE 5 Optical Activities of Bicycloazastannoxides

Entry	R	R'	Color	$[\alpha]_D^{20}$
1	Me	Bu	light yellow	−24 (c=0.3, CH_2Cl_2)
2	Me_2CHCH_2	Bu	light yellow	−50 (c=0.5, CH_2Cl_2)
3	$PhCH_2$	Bu	light yellow	−370 (c=0.5, CH_2Cl_2)
4	$MeS(CH_2)_2$	Bu	light yellow	−92 (c=0.5, CH_2Cl_2)
5	Me	Ph	yellow	−2 (c=1, CH_2Cl_2)
6	Me_2CHCH_2	Ph	yellow	−87 (c=1, CH_2Cl_2)
7	$PhCH_2$	Ph	yellow	−129 (c=1, CH_2Cl_2)
8	$MeS(CH_2)_2$	Ph	yellow	−52 (c=1, CH_2Cl_2)





The single crystal structure of "bicycloazastannoxide" 6

TABLE 6 Selected Bond Distances of Bicycloazastannoxide in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Sn	C (11)	2.124 (4)	C (24)	C (25)	1.383 (8)
Sn	C (21)	2.114 (4)	C (25)	C (26)	1.405 (8)
Sn	N	2.086 (3)	C (31)	C (32)	1.410 (8)
Sn	O (2)	2.137 (3)	C (31)	O (1)	1.317 (6)
C (11)	C (12)	1.375 (7)	C (32)	C (33)	1.386 (8)
C (11)	C (16)	1.406 (7)	C (33)	C (34)	1.435 (8)
C (12)	C (13)	1.396 (7)	C (34)	C (35)	1.390 (8)
C (13)	C (14)	1.387 (8)	C (35)	C (36)	1.426 (8)
C (14)	C (15)	1.382 (8)	C (36)	C (1)	1.427 (7)
C (15)	C (16)	1.393 (7)	C (1)	N	1.307 (7)
C (21)	C (22)	1.402 (7)	N	C (2)	1.467 (7)
C (21)	C (26)	1.410 (6)	C (2)	C (3)	1.518 (7)
C (22)	C (23)	1.398 (7)	C (3)	O (2)	1.291 (5)
C (23)	C (24)	1.401 (8)	C (3)	O (3)	1.212 (5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

The crystal was identified to be monoclinic, space group P21/c, β = 101.91 (**3**), Z = 4, D_c = 1.66 g/cm$_3$.

The single crystal structure was resolved by use of the MULTAN 82 program. The Sn atom was located from an E-map, and the coordinates of the remaining nonhydrogen atoms were found by sequence difference Fourier syntheses. It is shown in the following diagram that the Sn atom is situated in the center of a trigonal bipyramid, in which C, N and C atoms form an equatorial plane and two O atoms occupy the axial positions. A full matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms converged with unweighted and weighted discrepancy factors of 0.030 and 0.039, respectively. The highest peak on the final difference Fourier map had a height of 0.69 e/Å^3.

TABLE 7 Selected Bond Angles of Bicycloazastannoxide in Degrees

Atom 1	Atom 1	Atom 3	Angle
C (21)	Sn	C (11)	122.0 (2)
C (21)	Sn	N	106.6 (1)
C (21)	Sn	O (1)	99.1 (2)
C (21)	Sn	O (2)	98.7 (1)
C (11)	Sn	O (1)	92.4 (1)
C (11)	Sn	O (2)	92.5 (1)
C (11)	Sn	N	131.2 (2)
N	Sn	O (1)	90
O (1)	Sn	O (2)	180
O (1)	Sn	O (2)	180

5. Chemical investigation: (a) Attempted methylation of one of the bicycloazastannoxides (entry 7, Table 5) with MeI in benzene-ether solution gave no reaction after refluxing for 1 hour. After removal of the solvent, the yellow solid of complex 7 was recovered, the product isolated giving no melting point depression on admixture with the starting material. (b) Acid/base treatment resulted in degradation of the complex. The yellow color of the Complex (entry 7) in MeOH solution disappeared after dropwise addition of HCl; CO_2 was evolved, and the tin fragment became Ph_2SnCl_2. The addition of NaOH deepened the coloration of the solution; ultimately an amorphous precipitate of Ph_2SnO precipitated.

To test the aromatic properties of the heterocyclic ring, the reaction of complex 1 (Table 2) with Br_2 in methylene chloride solution was used. Iron powder was added to facilitate the electrophilic bromination. The color of the solution turned red. After the solution had been cooled a precipitate with mp 164–165° was collected. It was found to be the bromination product of the electrophilic substitution reaction.

DISCUSSION

Each of the bicycloazastannoxides has a low magnetic chemical shift of the hydrogens on the heterocyclic ring (δ = 8.30–8.50). It is speculated that the six-membered heterocyclic ring might possess aromatic character, but as mild electrophilic substitution with bromine does not affect this particular hydrogen ring, the metalloheterocyclic ring is deemed to be nonaromatic. On the other hand, the coordination of N→Sn seems quite stable. The nitrogen atom does not add a methyl group on treatment with MeI to form the pentacoordinate complex but remains as an imino complex.

The final hydrolysis product was found to be R_2SnX_2 or R_2SnO, depending upon the acidity of the medium [6]. The Schiff base may be recovered on basic hydrolysis, while acidic hydrolysis causes utter decomposition of the organic ligands.

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