anhydride (0.42 g, 2.0 mmol) in CH_2Cl_2 (12 m*l*) was stirred for 5 h at room temperature. The reaction mixture was washed with water (15 m*l*), dried ($MgSO_4$), and concentrated *in vacuo* to give anilide **IIu** (0.49 g, 92%): mp. 47-49°C ; ^1H NMR ($CDCl_3$) δ 3.40 (s, 3H, CH_3), 7.30 (d, 1H, Ph), 8.40 (d, 1H, Ph); MS m/e 355 (M^+, 30), 320 (85), 247 (100).

References

1. (a) G. Matolcsy, M. Nadasy, and V. Andriska, *Pesticide Chemistry*, Elsevier, Studies in Environmental Science 32 (1988); (b) D. R. Baker, J. G. Fenyes, and W. K. Moberg, *Synthesis and Chemistry of Agrochemicals II*, ACS Symposium Series 443, American Chemical Society, Washington D. C. (1991).
2. Methazole is a common name of 4-(3,4-dichlorophenyl)-2-methyl-oxadiazolidinone: for its metabolism see the references; (a) D. W. Jones and G. L. Foy, *Pestic. Biochem. Physiol.*, **2**, 8 (1972); (b) H. W. Dorough, R. A. Cardona, R. A. Cardona, and Lolmough, S. C.: *Drug Metabol. Disposition*, **2**, 129 (1974).
3. J. Kreuzer, US Patent 3437664; *Chem. Abstr.*, **71**, 38972x (1969).
4. L. Pauling and D. Pressman, *J. Am. Chem. Soc.*, **67**, 1003 (1945).
5. Activity (1 kg/ha)=0.009 MR^3−0.697 MR^2+14.811 MR−6.051.
6. G. Sato, E. Nagao, H. Oshio, and K. Kamoshita, *Pestic. Biochem. Physiol.*, **28**, 194 (1987).
7. in preparation and will be published elsewhere.
8. C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology*, Wiley, New York (1979).
9. E. Nagao, S. Hashimoto, R. Yoshida, H. Matsumoto, H. Oshino, and K. Kamoshita, Europe Patent 61741 (1982); *Chem. Abstr.*, **98**, 71924p (1983).
10. 2-Methyl-4-(2'-fluoro-4'-nitro-5'-methylphenyl)-1,2,4-oxadiazolidine-3,5-dione 7 was prepared from (2-fluoro-4-nitro-5-methyl-acetanilide 5 in a same manner to that described for (**IIa**).

Di- and Triorganotin(IV) Complexes of Sulfur-containing Ylidenemalonates

Ok-Sang Jung*, Young-A Lee, Jongki Hong†, Jong Hwa Jeong‡, and Youn Soo Sohn*

Inorganic Chemistry Laboratory

†*Advanced Analysis Center, Korea Institute of Science & Technology, Seoul 130-650*

‡*Department of Chemistry, Kyungpook National University, Taegu 702-701*

Organotin(IV) complexes of ylidenemalonates $(R_xSn)_y(O_2C)_2C=C(SR')_2$ (R = n-C_4H_9, C_6H_5, cyclo-C_6H_{11}, $CH_3OOCCH_2CH_2$; x=2,3; R'=CH_3, R_2'=-CHCH-, -CH_2CH_2-) have been synthesized and characterized by means of various spectroscopic methods. The X-ray crystal structure of $(Ph_3Sn)_2(O_2C)_2C=C(SCH_3)_2$ has been determined (Pī; a=9.704(2) Å, b=14.412 (1) Å, c=14.760(3) Å, α=74.26(1)°, β=99.38(1)°, γ=79.09(1)°, V=1950.7(7) $Å^3$) and refined to R=0.045. The crystal structure discloses a discrete molecule with bidentate-like carboxylate ligand. For diorganotin analogues, the structures are discussed in terms of IR, ^1H-NMR, ^{13}C-NMR, and FAB mass spectrometry. The mass spectrum indicates that the diorganotin complexes of ylidenemalonates are dimeric.

Introduction

Organotin carboxylates have received considerable attention because of industrial applicability such as homogeneous catalysts, agricultural biocides, and pharmaceutical properties[1-5] and in part because of various bonding modes of carboxylate ligands[6-8]. Even though a variety of papers on the organotin compounds of monocarboxylate ligand have been reported, dicarboxylate analogs have not been investigated extensively so far. In order to expand this chemistry this paper will describe the preparation and spectroscopic properties of the di- and triorganotin complexes of sulfur-containing ylidenemalonate ligands.

Experimental

Materials and Instruments. Organotin compounds were purchased from Alfa or Strem chemicals and used without further purification. $(CH_3OOCCH_2CH_2)_2SnCl_2$ was prepared by the literature method[9]. $(EtO_2C)_2C=C(SR)_2(R=CH_3, R_2=$-$CH_2CH_2$-, -CHCH-) were also prepared according to the known procedure[10,11] and hydrolyzed by the standard method.

Chemical analyses were carried out by the Advanced Analysis Center at KIST. Melting points were measured on

Table 1. Chemical Analysis and Spectroscopic Data

Compounds	Yield (%)	m.p. (℃)	Elemental Analysis Found (Calcd)		IR (cm⁻¹)		¹H-NMR δ (ppm)	¹³C-NMR (C=O) δ (ppm)
			C	H	ν(C=O)	ν(C=O)		
(Ph₃Sn)₂(O₂C)₂C=C(SCH₃)₂	85	126-128	55.70(55.67)	3.98(4.00)	1645		2.2(s, 6H), 7.2-7.7(m, 30H)	170.3
(Cy₃Sn)₂(O₂C)₂C=C(SCH₃)₂	87	106-108	54.10(53.52)	7.41(7.70)	1645		1.2-2.3(br, 66H), 2.4(s, 6H)	169.3
Cy₂Sn(O₂C)₂C=C(SCH₃)₂	82	161-165	44.40(44.04)	5.95(5.75)	1597		1.0-2.3(br, 22H), 2.4(s, 6H)	
n-Bu₂Sn(O₂C)₂C=C(SCH₃)₂	86	62-66	37.70(38.29)	5.58(5.51)	1562		1.7-2.0(m, 18H), 2.4(s, 6H)	172.1
(CH₃OOCCH₂CH₂)₂Sn(O₂C)₂ C=C(SCH₃)₂	85	80-83	33.60(33.69)	3.98(4.04)	1636	1734	1.8(t, J=4 Hz, 4H), 2.3(s, 6H), 2.8(t, J=4 Hz, 4H), 3.7(s, 6H)	171.7
(Cy₃Sn)₂(O₂C)₂C=C(SCH₂)₂	87	136-139	52.80(53.64)	7.28(7.50)	1617		1.2-2.3(m, 66H), 3.3(s, 4H)	
(CH₃OOCCH₂CH₂)₂Sn(O₂C)₂ C=C(SCH₂)₂	83	95	32.90(33.82)	3.78(3.65)	1546	1727	1.8(t, J=4 Hz, 4H), 2.8(t, J=4 Hz, 4H), 3.3(s, 4H), 3.7(s, 6H)	
(Cy₃Sn)₂(O₂C)₂=C(SCH)₂	87	118-122	52.90(53.75)	7.20(7.30)	1557		1.1-2.1(br, 66H), 7.7(s, 2H)	

a Thomas Hoover Capillary m.p. Appratus and were not corrected. The IR spectra in the 4000-400 cm⁻¹ region were measured on KBr pellet with MIDAC model 101025 FT-IR spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on Varian Gemini-300 NMR spectrometer or JEOL DMX 60 SI relative to SiMe₄ as an internal standard at ambient temperature. The mass spectrum was obtained from a VG hybrid mass spectrometer using a fast atom bombardment(FAB) mode. Cesium gun at 16 KV energy was used at neutral atom beam and glycerol was used as a matrix for FAB.

Synthesis. All title complexes were prepared by the following metathetic reaction of di- or triorganotin chloride with the potassium salt of the ylidenemalonate derivative in appropriate mole ratio.

(Ph₃Sn)₂(O₂C)₂C=C(SCH₃)₂. Triphenyltin chloride 3.85 g (10 mmol) and K₂(O₂C)₂C=(SCH₃)₂·2H₂O 1.58 g (5 mmol) in 40 m*l* of dichloromethane were stirred for 3 h at room temperature. The solution was filtered to remove potassium chloride, and the solvent was evaporated under vacuum to obtain a white solid of 3.85 g (85% yield). Recrystallization of the white solid from dichloromethane-ethyl alcohol solvent pair (1 : 2) gave colorless crystals (mp. 126-128℃) suitable for X-ray crystallography.

Crystallographic Analysis. All the crystallographic data were obtained on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated molybdenum radiation (λ(K_{α1})=0.70930 Å, λ(K_{α2})=0.71359 Å) at ambient temperature of 23± 2℃. Preliminary diffractometric investigation indicated triclinic P̄1(C_i^1, No. 2)¹² . Accurate cell dimensions were obtained from the setting angles of 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored after every 1 hour did not reveal any systematic variation in intensity. The data were corrected for Lorentz-Polarization effect, decay, and absorption with ψ-scan data. The structure was solved by conventional heavy atom method, followed by successive difference Fourier synthesis. The nonhydrogen atoms were refined anisotropically by using SHELX-76¹³ whereas the carbon atoms of phenyl rings were refined isotropically. Hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. Crystal parameters and procedural information corresponding to data collec-

Table 2. Crystal Data, Data collection, and Refinement of the Structure for (Ph₃Sn)₂(O₂C)₂C=C(SCH₃)₂

formula	C₄₂H₃₆O₄S₂Sn₂
fw	906.244
space group	P̄1
a, Å	9.704(2)
b, Å	14.412(1)
c, Å	14.760(3)
α, deg	74.26(1)
β, deg	99.38(1)
γ, deg	79.09(1)
V, Å³	1950.7(7)
Z	2
d_{calcd}, g cm⁻³	1.542
crystal size, mm	0.23×0.30×0.47
μ, cm⁻²	13.05
scan method	ω/2θ
data collected	h,± k,± l, 3<2θ<44
no. total observation	7224
no. unique data>3σ(I)	5235
no. parameters refined	235
abs. corr. factor range	0.9241-0.9998
gof	1.363
R=(Σ|F_o-F_c|)/Σ|F_o|	0.045
Rw=(Σ|F_o-F_c|w^{1/2})/Σ|F_o|w^{1/2}	0.055

$w=1.00/(\sigma^2(F)+0.002183\ F^2)$

tion and structure refinement are given in Table 2.

Results and Discussion

Synthesis. The reaction of di- or triorganotin chloride with ylidenemalonate smoothly afforded title compounds as shown in Eq. (1). Their elemental analyses and spectroscopic data are listed in Table 1. All the products are fairly airstable solids which are soluble in polar organic solvents such as chloroform, tetrahydrofuran, acetone, dimethyl formamide, and dimethyl sulfoxide.
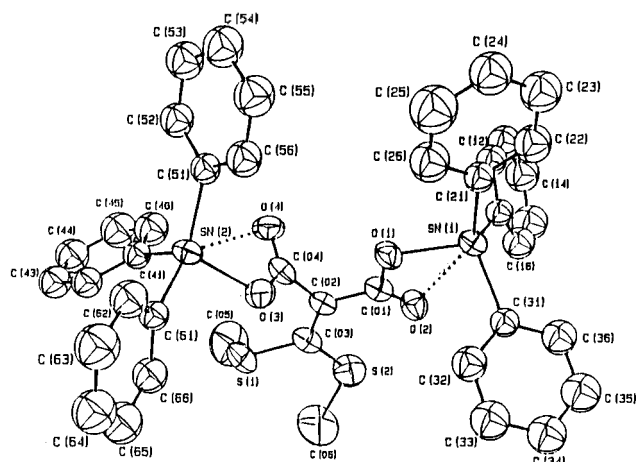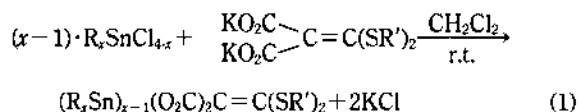
Figure 1. ORTEP drawing and labeling scheme of $(Ph_3Sn)_2(O_2C)_2$ $C = C(SCH_3)_2$ with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

$$(x-1) \cdot R_xSnCl_{4-x} + \begin{array}{c} KO_2C \\ KO_2C \end{array} C = C(SR')_2 \xrightarrow[\text{r.t.}]{CH_2Cl_2,}$$

$$(R_xSn)_{x-1}(O_2C)_2C = C(SR')_2 + 2KCl \qquad (1)$$

R: n-C_4H_9, C_6H_5, cyclo-C_6H_{11}, $CH_3OOCCH_2CH_2$
x: 2,3
R': CH_3, R'_2: -CH_2CH_2-, -CHCH-

Crystal Structure of $(Ph_3Sn)_2(O_2C)_2C = C(SCH_3)_2$.
The molecular structure and atomic labeling scheme are shown in Figure 1, and selected bond distances and bond angles are listed in Table 3. The complex is a discrete molecule with no close intermolecular contacts (the shortest distance of intermolecule in 3.40(1) Å of $C(05) \cdots O(2)$) whereas triphenyltin acetate has been elucidated as a polymeric chain[14]. Another interesting feature of the structure is the bonding mode of carboxylate ligand. The $Sn(1)-O(1)$ (2.057(4) Å) and $Sn(2)-O(3)$ (2.052(5) Å) distances are typical value of Sn-O covalent bond distance(see Table 4). However, the distances of $Sn(1) \cdots O(2)$ (2.747(4) Å) and $Sn(2) \cdots O(4)$ (2.855(4) Å) are considerably longer than the normal values of Sn-O distance although the distances between tin and pendant oxygen atom are much shorter than the Van der waals radii for Sn and O of 3.7 Å. The X-ray structural data of some related monomeric organotin carboxylates are listed in Table 4. Table 4 lists 13 structures in grouping in order of increasing of bond strength between tin and pendant oxygen. The pendant $O \cdots Sn$ distances of the present structure are median values between two limiting structures of $Cy_3Sn(O_2CCF_3)(Sn \cdots O(2)$, 3.11(4) Å) and $Ph_3Sn(O_2C)(C_6H_4(N_2C_6H_3(OH)(CH_3)))$ $(Sn \cdots O(2)$, 2.463(7) Å). Thus, the local geometry of the tin atom can hardly be discerned with certainty solely by X-ray data. However, the local geometries of $Sn(1)$ and $Sn(2)$ approximate to that of $Ph_3Sn(O_2CC_4H_3S)^{22}$ and $Ph_3Sn(O_2CC_6H_4Cl-p)$,[19] respectively. Therefore the carboxylate ligand of the present structure seems to be bidentate-like, and thus tin atom environment may be best described as pseudo trigonal bipyramid.

Spectroscopic Properties. The ^{1}H-NMR data for the present compounds are consistent with the expected struc-

Table 3. Bond Distances (Å) and Bond Angles (°) for $(Ph_3Sn)_2$ $(O_2C)_2C = C(SCH_3)_2$

$Sn(1) \cdots O(1)$	2.057(4)	$Sn(1) \cdots O(2)$	2.747(4)
$Sn(1) \cdots C(11)$	2.117(4)	$Sn(1) \cdots C(21)$	2.133(4)
$Sn(1) \cdots C(31)$	2.117(4)	$Sn(2) \cdots O(3)$	2.052(4)
$Sn(2) \cdots O(4)$	2.855(4)	$Sn(2) \cdots C(41)$	2.124(4)
$Sn(2) \cdots C(51)$	2.115(4)	$Sn(2) \cdots C(61)$	2.127(4)
$S(1) \cdots C(03)$	1.761(6)	$S(1) \cdots C(05)$	1.778(10)
$S(2) \cdots C(03)$	1.753(6)	$S(1) \cdots C(06)$	1.767(9)
$O(1) \cdots C(01)$	1.316(6)	$O(2) \cdots C(01)$	1.224(7)
$O(3) \cdots C(04)$	1.301(7)	$O(4) \cdots C(04)$	1.219(7)
$C(01) \cdots C(02)$	1.472(7)	$C(02) \cdots C(03)$	1.342(7)
$C(02) \cdots C(04)$	1.496(8)		
$O(1)-Sn(1)-O(2)$	52.6(2)	$C(03)-C(02)-C(01)$	124.5(5)
$C(11)-Sn(1)-O(1)$	111.2(2)	$C(04)-C(02)-C(01)$	115.6(4)
$C(21)-Sn(1)-O(1)$	98.1(1)	$C(04)-C(02)-C(03)$	119.9(5)
$C(21)-Sn(1)-C(11)$	108.8(2)	$S(2)-C(03)-S(1)$	120.2(3)
$C(31)-Sn(1)-O(1)$	104.0(1)	$C(02)-C(03)-S(1)$	117.8(5)
$C(31)-Sn(1)-C(11)$	117.9(1)	$C(02)-C(03)-S(2)$	122.0(5)
$C(31)-Sn(1)-C(21)$	114.8(2)	$O(4)-C(04)-O(3)$	122.4(5)
$O(3)-Sn(2)-O(4)$	50.3(1)	$C(02)-C(04)-O(3)$	115.1(5)
$C(41)-Sn(2)-O(3)$	108.9(2)	$C(02)-C(04)-O(4)$	122.4(5)
$C(51)-Sn(2)-O(3)$	111.3(2)	$C(12)-C(11)-Sn(1)$	117.4(1)
$C(51)-Sn(2)-C(41)$	116.9(1)	$C(16)-C(11)-Sn(1)$	122.5(1)
$C(61)-Sn(2)-O(3)$	96.0(2)	$C(22)-C(21)-Sn(1)$	118.6(1)
$C(61)-Sn(2)-C(41)$	108.8(1)	$C(26)-C(21)-Sn(1)$	121.4(1)
$C(61)-Sn(2)-C(51)$	112.8(1)	$C(32)-C(31)-Sn(1)$	120.1(1)
$C(05)-S(1)-C(03)$	102.9(5)	$C(36)-C(31)-Sn(1)$	119.9(1)
$C(06)-S(2)-C(03)$	104.6(5)	$C(42)-C(41)-Sn(2)$	117.4(1)
$C(01)-O(1)-Sn(1)$	108.0(3)	$C(46)-C(41)-Sn(2)$	122.5(1)
$C(04)-O(3)-Sn(2)$	111.3(4)	$C(52)-C(51)-Sn(1)$	119.3(1)
$O(2)-C(01)-O(1)$	121.6(5)	$C(56)-C(51)-Sn(1)$	120.5(1)
$C(02)-C(01)-O(1)$	114.5(5)	$C(62)-C(61)-Sn(1)$	120.9(1)
$C(02)-C(01)-O(2)$	124.0(5)	$C(66)-C(61)-Sn(2)$	118.8(1)

Table 4. Structural Parameters for $R_3Sn(O_2CR')$

R	R'	Sn-O(1)	Sn-O(2)	Ref.
cyclo-C_6H_{11}	CF_3	2.08(4)	3.11(4)	15
C_6H_5	C_6H_4OH-o	2.083(2)	3.07(2)	16
cyclo-C_6H_{11}	CH_3	2.12(3)	2.95(4)	17
cyclo-C_6H_{11}	$CH_2(C_8H_6N)^a$	2.086(3)	2.929(4)	18
C_6H_5	C_6H_4Cl-p	2.048(4)	2.861(4)	19
C_6H_5	$C_6H_4NH_2$-o	2.043(3)	2.823(3)	20
C_6H_5	$C_6H_4SCH_3$-p	2.060(2)	2.783(3)	16
C_6H_5	$C_6H_4OCH_3$-o	2.054(3)	2.781(3)	16
cyclo-C_6H_{11}	$CH_2(C_8H_6NCH_3)^b$	2.05(1)	2.78(1)	21
C_6H_5	C_4H_3S	2.076(4)	2.768(4)	22
C_6H_5	$C_6H_4N(CH_3)_2$-p	2.072(2)	2.629(2)	20
C_6H_5	$C_6H_4N(CH_3)_2$-o	2.115(6)	2.564(7)	20
C_6H_5	$C_6H_4(N_2C_6H_3(OH)(CH_3))^c$	2.070(5)	2.463(7)	23

^{a} Indole-3-acetic acid, ^{b} N-methylindole-3-acetic acid, ^{c} o-(2-Hydroxy-5-methylphenylazo)benzoate
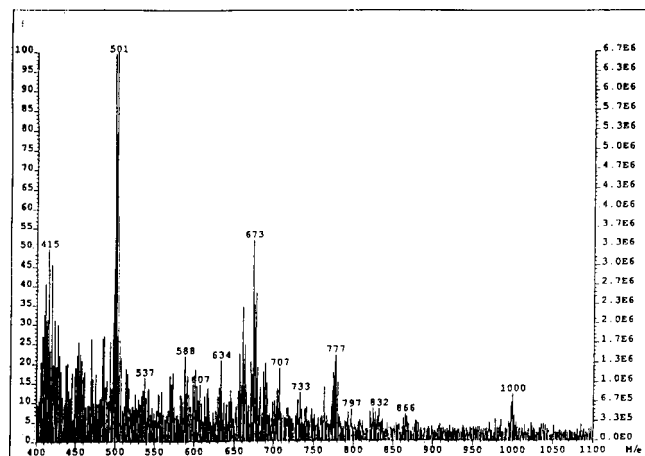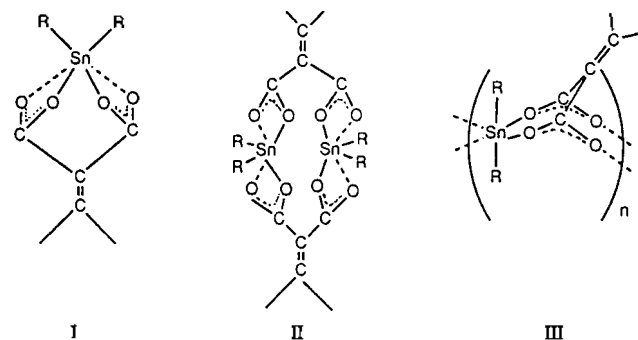
Figure 2. FAB mass spectrum of $[(CH_3OOCCH_2CH_2)_2Sn(O_2C)_2C=C(SCH_2)_2]_2$.

tures. In particular, for $(CH_3OOCCH_2CH_2)_2Sn(O_2C)_2C=C$ $(SCH_3)_2$ and $(CH_3OOCCH_2CH_2)_2Sn(O_2C)_2C=C(SCH_2)_2$ the ^1H resonance for the CH_3O- group (3.7 ppm) shows upfield shift by about 0.2 ppm compared to that of the chelated ester group in $(CH_3OOCCH_2CH_2)_2SnCl_2^{24}$, implying that the two ester groups of each compound are not coordinated to tin owing presumably to accommodate the carboxylate ligands. This fact strongly suggests that the bonding fashion of the carboxylate ligand is not simple monodentate but bidentate-like even in solution. ^{13}C-NMR also explains the bonding character of the carboxylate group. The ^{13}C chemical shift (169.3 ppm) of the carboxylate in $(Cy_3Sn)_2(O_2C)_2C=C(SCH_3)_2$ exhibits upfield shift by 1.0 ppm relative to that (170.3 ppm) in triphenyltin analog. Such a shielding supports that the bidentate character of carboxylate in $(Cy_3Sn)_2(O_2C)_2C=C$ $(SCH_3)_2$ is relatively decreased, due probably to the steric and electronic effect of cyclohexyl group. Furthermore, the ^{13}C resonances of diorganotin analogs, $(n-Bu)_2Sn(O_2C)_2C=C$ $(SCH_3)_2$ (172.1 ppm) and $(CH_3OOCCH_2CH_2)_2Sn(O_2C)_2C=C$ $(SCH_3)_2$ (171.7 ppm) are deshielded by 1.4-2.8 ppm relative to above triorganotin analogs, exhibiting that carboxylate of diorganotin compound is more bidentate-like than that of triorganotin compound. Assuming from the above-mentioned spectroscopic data that the carboxylate ligand acts as bidentate-like, following three distinct structures I(monomeric), II (dimeric), and III(polymeric) can be proposed for the present diorganotin compounds. FAB mass spectrum (Figure 2) for $(CH_3OOCCH_2CH_2)_2Sn(O_2C)_2C=C(SCH_3)_2$ suggests that this compound is a dimeric form. The mass spectrum was scan-

ned from 400 up to 1500 a.m.u., but no ions were detected beyond $m/e=1000$. The spectrum shows the molecular ion of the dimer form $[(CH_3OOCCH_2CH_2)_2Sn(O_2C)_2C=C(SCH_3)_2]_2$ at $m/e=1000$. Also shown is a monomeric ion $(CH_3OOCCH_2$-$CH_2)_2Sn(O_2C)_2C=C(SCH_3)_2$, at $m/e=500$ which may be a fragment from dimeric parent ion. The complexity of the spectrum actually arises from a complicated isotopic pattern of tin itself. The IR data of the present compounds show the strong carboxylate bands in the range of 1518-1645 cm^{-1}, but they do not give the conclusive information for the structure because of complexness in the region. However, in case of diestertin compounds, the carbonyl stretching frequencies of ester groups (1734 cm^{-1} for $(CH_3OOCCH_2CH_2)_2Sn(O_2C)_2$ $C=C(SCH_3)_2$; 1727 cm^{-1} for $(CH_3OOCCH_2CH_2)_2Sn(O_2C)_2C=$ $C(SCH_2)_2$) are strongly indicative of free ester groups.

References

1. A. G. Davis and P. J. Smith, in G. Wilkinson, F. G. A. Stone and E. W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, Vol. 2, 1982.
2. C. J. Evans and S. Karpel, Organotin Compounds in Modern Technology, J. Organomet. Chem. Lib. 16, Elsevier, Amsterdam, 1985.
3. S. J. Blunden and A. Chapman, in P. J. Craig (Ed.), Organotin Compounds in the Environment, Organometallic Compounds in the Environment, Longman, Harlow, 19 86.
4. I. Omae, Organotin Chemistry, J. Organomet. Chem. Lib. 21, Elsevier, Amsterdam, 1989.
5. A. J. Crowe, The Antitumor Activity of Tin Compounds in M. F. Gielen (Ed.), Metal-Based Anti-tumor Drugs, p. 103, Freund Publishing House LTD, London, 1988.
6. E. R. T. Tiekink, Appl. Organomet. Chem., **5**, 1 (1991).
7. R. R. Holmes, Acc. Chem. Res., **22**, 190 (1989).
8. V. Chandrasekhar, C. G. Schmid, S. D. Burton, J. M. Holmes, R. O. Day, and R. R. Holmes, Inorg. Chem., **26**, 1050 (1987).
9. R. E. Hutton and V. Oakes, in J. J. Zuckerman (Ed.), Organotin Compounds: New Chemistry and Applications, Advances in Chemistry Series, Vol. 157, p. 123, American Chemical Society, Washington DC, 1976.
10. E. Söderbäck, Acta Chem. Scand., **17**, 363 (1963).
11. N. Katagiri, S. Ise, N. Watanabe, and C. Kaneto, Chem. Pharm. Bull., **38**, 3242 (1990).
12. International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, U.K. 1974.
13. G. M. Sheldrick, SHELX 76: Program for Crystal Structure Determination, University of Cambridge, U.K. 1976.
14. K. C. Molloy, T. G. Purcell, K. Quill, and I. W. Nowell, J. Organomet. Chem., **267**, 237 (1984).
15. S. Calogero, P. Ganis, V. Peruzo, and G. Tagliavini, J. Organomet. Chem., **191**, 381 (1980).
16. J. F. Vollano, R. O. Day, D. N. Rau, V. Chandrasekhar, and R. R. Holmes, Inorg. Chem., **23**, 3153 (1984).
17. N. W. Alcock and R. E. Timms, J. Chem. Soc. A., 1876 (1968).
18. K. C. Molloy, T. G. Purcell, E. Hahn, H. Schumann, and J. J. Zuckerman, Organometallics, **5**, 85 (1986).

I   II   III

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19. R. R. Holmes, R. O. Day, V. Chandrasekhar, J. F. Vollano, and R. R. Holmes, *Inorg. Chem.*, **25**, 2490 (1986).
20. R. G. Swisher, J. F. Vollano, V. Chandrasekhar, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **23**, 3147 (1984).
21. K. C. Molloy, T. G. Purcell, M. F. Mahon, and E. Minshall, *Appl. Organomet. Chem.*, **1** 507 (1987).

22. S. W. Ng, V. G. Kumar Das, F. Van Meurs, J. D. Schagen, and L. H. Straver, *Acta Crystallogr. C.*, **45**, 568 (1989).
23. P. G. Harrison, K. Lambert, T. J. King, and B. Majee, *J. Chem. Soc., Dalton Trans.*, 363 (1983).
24. O. S. Jung and Y. S. Sohn, Unpublished result.

Complexation of Cadmium(II) with Humic Acids: Effects of pH and Humic Acid Origin

Mee Hae Lee, Se Young Choi, Kun Ho Chung, and Hichung Moon*

Department of Chemistry, Korea Advanced Institute of Science and Technology
373-1 Kusong dong, Yusong ku, Teajun-shi 305-701

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A comparative study on cadmium (II) complexation with three well characterized humic acids (SHA: soil humic acid from the Okchun Metamorphic Belt; AqHA: aquatic humic acid from Gorleben underground aquifer, Germany; CoHA: commercially available humic acid from the Aldrich Co.) was carried out in 0.1 M NaClO₄ at different solution pH (5.0, 5.5, and 6.0) using the ultrafiltration technique. The maximum binding ability (MBA) of the humic acids for cadmium (II) was observed to vary with their origins and solution pH. The results suggest that 1 : 1 complex predominates within the experimental range, and the conditional stability constants were calculated based on the assumption of cooperative binding, yielding $\log K$ values that were quite similar (CoHA: 4.17 ± 0.08; AqHA: 4.14 ± 0.07; SHA: 4.06 ± 0.12 l mol^{-1} at pH 6.0) irrespective of humic acid origins or pH. By contrast a nonlinear Schatchard plot was obtained, using the cadmium (II) ion selective electrode speciation analysis method, which indicated that humic acid may have two or more classes of binding sites, with $\log K_1$ and $\log K_2$ of 4.73 ± 0.08 and 3.31 ± 0.14 l mol^{-1} respectively.

Introduction

Cadmium toxicity is of great environmental concern in the rapidly industrializing nations of the East Asian region. Due to increased industrial usage and related mining activities, elevated levels of cadmium are found in terrestrial and aquatic environments[1]. During the hot summer season, torrential downpour of monsoon rain causes floodwater to flush away much of soil organic matters and other pollutants into river systems and subsequently into flooded rice fields[2]. Well documented cases of itai-itai desease in the neighbouring Japan are known to be caused by eating cadmium contaminated rice grown on polluted lands[3].

In natural aquifer systems the salinity, water hardness and pH are known to affect the cadmium speciation. However, the naturally occurring organic matters in freshwater systems such as humic and fulvic acids (HA and FA) are known to possess high affinity for metal cations ($Z \geq 2+$) and can also affect the cadmium speciation[4,5]. Two parameters are required for the quantification of the migrational behaviour and availability of trace metals in freshwater systems. They are 1) basic understanding on the nature of humic acids, and 2) determination of the conditional stability constants. The reviews on these topics are reported in the literature[6,7]. Many factors can influence the results of complexation studies between humic substances and trace metal ions. One such factor is the variable nature of humic acid; humic acid extracted from different source materials is different and depends on botanic and climatic conditions, age, and depth of burial. Other factors include relative humic acid to metal ion concentrations, ionic strength, pH, method of speciation analysis, and model used to describe the complexation behaviours[8].

In this work, the results of the studies on the complexation of cadmium (II) with three different humic acids of differing origins conducted at pH of 5.0, 5.5 and 6.0 are described. The investigations were conducted at constant ionic strength ($I = 0.1$) and at humic acid concentrations typically found in summer storm floodwaters (50 and 100 mg l^{-1}) resulting from monsoon rain. Both the separation and nonseparation methods of speciation analysis were used for these investigations, namely ultrafiltration technique (UF, separation) and cadmium (II) ion selective electrode (Cd(II)-ISE, nonseparation). In using the ultrafiltration method, the effects of sorption of labile metal ions on the filter membrane and equilibria shift during the separation stage were minimized by using appropriately designed apparatus and suitable membrane filters[9,10]. Two models were used to graphically illustrate the experimental data: 1) a positive cooperative binding model based on the Hill plot (1 : 1 complex predominates) and 2) a Schatchard plot which assumes that there are two or more classes of binding sites[11].