X-ray Crystal and Molecular Structure of the Dimeric 1:1 Dimethyltin(IV) Dichloride Adduct with Diphenylcyclopropenone, $[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$, at 138 ± 2 K

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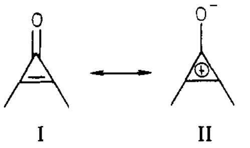
Abstract: Dimethyltin(IV) dichloride–diphenylcyclopropenone, $C_{34}H_{32}Cl_4O_2Sn_2$, forms colorless crystals, mp 111 °C, in the monoclinic space group $C2/c$ with $a = 17.049$ (16) Å, $b = 10.027$ (10) Å, $c = 19.834$ (16) Å, $\beta = 96.00$ (6)°, $V = 3372$ Å^3, $Z = 4$, $\rho_{calcd} = 1.678$ g cm^{-3}. The structure was determined by the heavy atom method from 4890 reflections measured at 138 ± 2 K on an Enraf-Nonius CAD/4 automatic diffractometer with monochromatic Mo Kα radiation to a final R value of 0.0296 for the 4251 reflections included in the least-squares sums. The dimeric molecule contains six-coordinated tin with the oxygen atom of the ligand and one chlorine atom in a trans position making a Cl(1)–Sn–O angle of 172.32 (5)°. The angle made by the methyl groups is opened to 142.2 (1)°, and the octahedron is completed by a roughly trans Cl(2)–Sn–Cl(1′) angle of 166.10 (2)°. The Sn_2Cl_2 ring is formed by bonded [d(Sn–Cl(1)) = 2.4745 (7) Å] and bridging [d(Sn–Cl(1′)) = 3.5607 (7) °Å] connections. The tin atom lies 0.0266 (2) Å above the plane formed by the carbons of its two methyl groups, its terminally bonded chlorine [Cl(2)], and the chlorine atom bridged to it [Cl(1′)], in the direction of the Cl(1) atom. The shortest bond is made to the terminal chlorine [d(Sn–Cl(2)) = 2.3713 (6) Å]. The distances in the $Sn{\leftarrow}O{=}C$ system [2.380 (2) and 1.239 (3) Å, respectively] reflect a normal carbonyl unit, but the intraring distances, d(C=C) and d(C—C) [1.376 (3) and 1.397 (3), 1.402 (3) Å, respectively], and C—C(O)—C angle [58.9 (2)°] reflect a more delocalized situation than in the free diphenylcyclopropenone. The ligand system is relatively flat, with the phenyl rings tilted out of the plane of the cyclopropenone system by 2.5° and 8.4°. The angle formed by the ligand oxygen and three-carbon ring and the plane containing the $C{=}O{\rightarrow}Sn$ system is 11.7 (2)°. The Sn_2Cl_2 ring is almost flat, being bent through dihedral angles of 2.25 (3)°. The sum of the internal angles is 359.94°, with acute angles at the tin atoms 77.26 (2)° and open angles at the chlorines 102.71 (2)°. Each monomeric unit is related to its other half by a twofold axis.

Cyclopropenones,[1] of which to date only the diphenyl derivative has been extensively studied, are much more basic than other ketones, even other α,β-unsaturated ketones, owing to the availability of resonance forms that place negative charge on the oxygen:



(1)

This gives rise to an enhanced dipole moment ($\mu = 5.08$ D[2] vs. 2.85 D for acetone[3]) and the formation of a stable solid monohydrate, mp 87.5 °C,[4] not generally formed by aromatic ketones. The molecular structure of the anhydrous solid is known from X-ray studies[5] and the gas-phase species from microwave.[6] Independent X-ray determinations of the structure of the hydrate show half the molecules in the crystal hydrogen bonded to one and half to two water molecules but disagree on the details of the ring dimensions.[7,8] Another X-ray study of bis(p-chlorophenyl)cyclopropenone[9] has been critized as giving erroneous results.[8]

It would be expected that the contribution of II would be successively enhanced by hydrogen bonding of the carbonyl oxygen atom to one and then two water molecules. Structure II would also be expected to predominate in complexes with metal centers of which derivatives with divalent zinc, cobalt, nickel, copper, ruthenium, palladium, and platinum halides,[10] rhodium(III) halides,[10] cobalt and platinum carbonyls,[11] and antimony pentachloride[12] are known. All are coordinated through oxygen from infrared evidence, but no structural data have hitherto been available.

Mixing chloroform solutions of diphenylcyclopenone and dimethyltin(IV) dichloride yields a 1:1 adduct, $(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2$, mp 111 °C dec.[13] Lowering of the infrared band at 1640 cm^{-1} [14] in the free ligand reflects bonding through the carbonyl, and the NMR ($|^2J(^{119}Sn{-}C{-}^1H)| = 77.7$ Hz) in chloroform reflects the higher coordination number produced at the tin atom.[13] The tin-119m Mössbauer parameters [isomer shift (IS) = 1.41; quadrupole splitting (QS) = 3.52 mm s^{-1}] were interpreted in terms of a five-coordinated, trigonal-bipyramidal geometry at tin in which the ligand is axially positioned, opposite one chlorine, based upon the additivity of electric field gradients.[15]

Aldehydes and ketones are generally weak donors toward tin, and the isolable complexes usually involve ligands with the capacity for charge dispersal. Diorganotin(IV) dihalides can form either

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[†] University of Oklahoma.
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Table I. Crystal Data for $[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$

formula	$C_{34}H_{32}Cl_4O_2Sn_2$
formula wt	831.84
cryst system	monoclinic
a, Å	17.049 (16)
b, Å	10.027 (10)
c, Å	19.834 (16)
β, deg[a]	96.00 (6)
V, Å^3	3372
space group	$C2/c$[b]
Z	4
$F(000)$	1680
ρ(calcd), g cm^{-3}	1.678
μ, cm^{-1}	18.34
dimens of data crystal, mm	0.18 × 0.33 × 0.48
T(max), T(min)	0.72, 0.41

[a] From $\pm 2\theta$ values of reflections with the use of Mo K$\bar{\alpha}_1$ radiation ($\lambda = 0.70926$ Å). [b] Based upon systematic absences: h,k,l: $h + k = 2n + 1$; $h,0,l$: $l = 2n + 1$.

1:1 or 1:2 adducts with donor molecules. The choice depends upon the interplay of a complex mix of discernable factors, inter alia, the basicity of the coordinating atom or steric effects, which may originate on the tin moiety or the donor molecule. In the latter, whether the donor atom is terminally attached as part of a pointed group, as in the carbonyl group of an aldehyde or ketone or in a $>C{=}S$-, $>S{=}O$-, $\rightarrow P{=}O$-, or $\rightarrow N \rightarrow O$-containing ligand, is apparently important,[16] as is the possibility for chelation. The generation of ionic charges or strong dipoles in the resulting product must also play a role. Of course, the stoichiometry of the reactants and the conditions of the synthesis will have an influence, but it is surprising that the variation of these parameters is not more often determining. Using current knowledge it is not possible to predict whether a 1:1 or 1:2 complex will form under any given set of circumstances. Known adducts, even disregarding ancient claims, present a confused picture. For example, triphenylphosphine oxide, a strongly basic, pointed ligand forms 1:2 adducts with dimethyl-, methylphenyl- and dibenzyltin(IV) dichloride, but only a 1:1 complex with divinyltin(IV) dichloride.[13] Both 1:1 and 1:2 adducts are isolated with diphenyltin(IV) dichloride.[17,18] The presumably less basic, also pointed ligand, diphenylcyclopropenone, on the other hand, forms 1:1 adducts with divinyltin(IV) dichloride.[13] It is curious that the sterically undemanding pointed ligands, which should allow complexation to proceed to the 1:2 products, are the ones that form the 1:1 complexes instead.

One structure report is available for a 1:1 complex of dimethyltin(IV) dichloride,[19] and the ligand is described as being attached through a $CH{=}O$ group. Although the salicylaldehyde donor is capable of chelation through the phenolic OH, this group hydrogen bonds to its aldehydic oxygen neighbor. The geometry about the tin center is interpreted as a badly distorted trigonal bipyramid, with the ligand oxygen axial with one of the chlorines and the two methyl groups and second chlorine atom equatorial.[20] In the 1:1 adduct of dimethyltin(IV) dichloride with pyridine N-oxide, infrared and Raman evidence was used to suggest an equatorial position for the ligand in a trigonal-bipyramidal geometry.[21,22]

We report in this paper the structure of the 1:1 adduct of diphenylcyclopropenone with dimethyltin(IV) dichloride. A preliminary report, describing inter alia this result, has been communicated.[24]

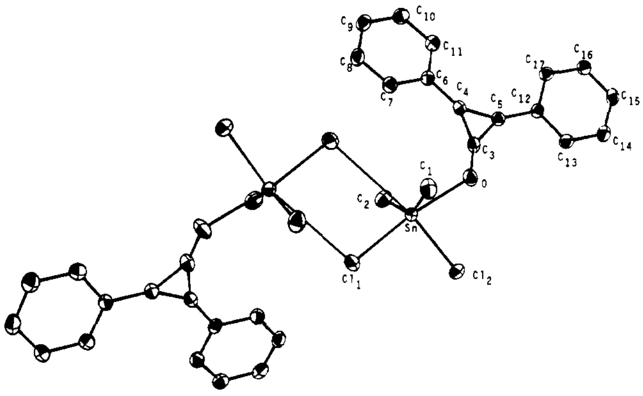

Figure 1. Asymmetric unit of $[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$ showing the atom numbering.

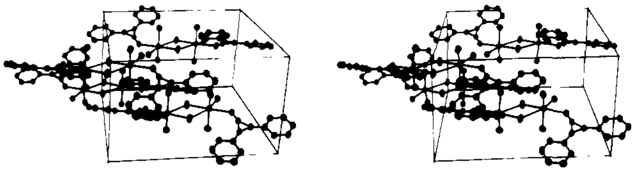

Figure 2. Unit cell contents of $[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$.

Experimental Section

Synthesis of the Dimethyltin(IV) Dichloride–Diphenylcyclopropenone Dimer, $[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$.[13] Diphenylcyclopropenone was synthesized by the method of Breslow and Posner.[25] Concentration of a chloroform solution of dimethyltin(IV) dichloride (2.20 g, 10.0 mmol) and diphenylcyclopropenone (4.12 g, 20.0 mmol) gave a white precipitate, which was recrystallized from chloroform to give the 1:1 adduct, mp 109–111 °C, in 70% yield. Single crystals of the compound that melted sharply at 111 °C were obtained by slow evaporation of a chloroform solution. Upon exposure to air for a few hours, however, a white powder formed on the surfaces of the crystals, which made them unsuitable for collecting data. The compound is soluble in the common dense organic solvents, and its exact density could, as a consequence, not be determined.

Crystal Data. Data were obtained at 138 ± 2 K with an Enraf-Nonius CAD/4 automatic counter diffractometer controlled by a PDP-8/e computer and fitted with a low-temperature apparatus. Crystal data are listed in Table I.

Details of our diffractometer and methods of data reduction have been outlined previously.[26] Specific parameters pertaining to the collection of this data set are summarized in Table II. The structure factors for each reflection were assigned weights on the basis of counting statistics.[26]

Structure Determination and Refinement. Systematic absences gave two possible space groups, $C2/c$ and Cc, and since a distinction could be made from the Patterson map, the structure was refined in the former. The positions of the tin and chlorine atoms were determined from a three-dimensional Patterson map. Structure factors calculated with Sn and Cl parameters gave an R factor ($R = \sum||kF_o| - |F_c||/\sum|kF_o|$) that was refined to 0.260, and a difference Fourier map was then calculated. From the difference map, all non-hydrogen atoms were located. These atoms were refined isotropically and then anisotropically to an R factor of 0.0351 for 4251 reflections by using a block-diagonal least-squares program.[27] A difference Fourier map calculated at this stage revealed all hydrogen positions. Hydrogen atoms were refined isotropically. The effect of anomalous dispersion by the tin and chlorine atoms was included in F_c by using $\Delta f'$ and $\Delta f''$ from ref 28. Refinement was discontinued when the maximum parameter shift for all the atoms was less than one-sixth of the corresponding standard deviation. The final R factor is

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Table II. Data Collection Parameters for $[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$

diffractometer	Enraf-Nonius CAD/4
radiation	Mo K$\bar{\alpha}$ (λ = 0.71069 Å)
temp, K	138 ± 2
scan technique	θ–2θ
2θ limit, deg	0 < 2θ < 60
max scan time, s	50
scan angle, deg	0.8 + 0.2 tan θ
aperture width, deg	3.5 + 0.86 tan θ
aperture height, mm	6
aperture dist, mm	173
monitor reflctn	3
intens monitors	3
max fluctuation in monitor, %	<3.0
orientation monitors	200 reflctn[a]
no. of unique data	4890
no. of obsd data	4251
corrections	Lorentz-polarization anomalous dispersion

[a] New orientation matrix if angular change >0.1°. Orientation matrix based upon 17 reflections. [b] $I > 2\sigma(I)$.

Table III. Final Positional Parameters (Å) for the Dimethyltin(IV) Dichloride–Diphenylcyclopropenone Dimer (×10^4)[a]

atoms	x	y	z
Sn	1351.3 (1)	2113.5 (2)	2294.6 (1)
Cl(1)	100.9 (4)	2160.7 (8)	1539.3 (4)
Cl(2)	2099.0 (4)	1727.1 (7)	1370.5 (3)
O	2639 (1)	2136 (2)	2889 (1)
C(1)	1254 (2)	213 (3)	2742 (2)
C(2)	1305 (2)	4172 (3)	2508 (2)
C(3)	2916 (1)	2673 (2)	3424 (1)
C(4)	2849 (1)	3336 (2)	4035 (1)
C(5)	3586 (1)	3017 (2)	3860 (1)
C(6)	2369 (1)	3916 (2)	4521 (1)
C(7)	1550 (1)	3854 (3)	4388 (1)
C(8)	1071 (1)	4425 (3)	4834 (1)
C(9)	1405 (2)	5062 (3)	5412 (1)
C(10)	2218 (2)	5113 (3)	5553 (1)
C(11)	2703 (1)	4549 (3)	5112 (1)
C(12)	4429 (1)	2961 (2)	4003 (1)
C(13)	4870 (2)	2434 (3)	3508 (1)
C(14)	5682 (2)	2305 (3)	3642 (1)
C(15)	6051 (1)	2677 (3)	4271 (2)
C(16)	5615 (1)	3199 (3)	4765 (1)
C(17)	4807 (1)	3355 (3)	4634 (1)

[a] Estimated standard deviations in parentheses.

0.0296 for the 4251 reflections that were included in the least-squares calculations and is 0.0391 for all 4890 reflections. The final difference Fourier map was essentially featureless except around the tin atom, where peak heights up to 1.3 e Å^{-3} still persisted. These residual peaks are ascribed to ripples originating from the tin atom.

The scattering factors used were for neutral atoms and were taken from ref 28 (Sn, C, O, and Cl) and 27 (H).

Final atomic parameters (positional and thermal) are given in Tables III and IV, respectively, and final interatomic distances and angles are given in Tables V and VI, respectively. Hydrogen parameters are given in Table VII, and carbon and hydrogen distances and angles are listed in Table VIII. The asymmetric unit (with atom numbering scheme) is shown in Figure 1, and the arrangement of molecules within the unit cell in Figure 2. The equations of the least-squares planes and the deviations from these planes are listed in Table IX.

Description and Discussion of the Structure

The 1:1 nature of the complex is confirmed in the structure depicted in Figure 1, but the adduct molecules are seen to form a dimer through intermolecular chlorine bridging. At the center of the dimer is an almost planar Sn_2Cl_2 ring formed by longer [d(Sn–Cl(1′) = 3.5607 (7) Å] and shorter [d(Sn–Cl(1)) = 2.4745 (7) Å] tin–chlorine bonds. The shortest connection is made to a terminal chlorine atom [d(Sn–Cl(2)) = 2.3713 (6) Å], which lies roughly trans to the chlorine atom [Cl(1′)] bridging from the second molecule at 166.10 (2)°. The angle made by the methyl groups is opened to 142.2 (1)°, but the largest angle at tin is formed by the Cl(1)–Sn–O system at 172.32 (5)°. Each monomeric unit is related to its other half by a twofold axis. The angles at the tins are acute [77.26 (2)°] in the Sn_2Cl_2 ring, while the angles at the chlorines are open [102.71 (2)°]. The entire diphenylcyclopropenone system is almost flat, and space is filled by packing the complexes in parallel planes with tin atoms on the same side in each layer, as shown in Figure 2. This direction is reversed in alternate layers. Such packing allows the tin atom to adopt the conventional octahedral geometry for six-coordination with the carbonyl oxygen trans to one chlorine atom.

Table V. Intramolecular Distances (in Å) in $[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$[a]

Sn–Heteroatom Distances	
Sn–Cl(1)	2.4745 (7)
Sn–Cl(2)	2.3713 (6)
Sn–C(1)	2.116 (3)
Sn–C(2)	2.111 (3)
Sn–O	2.380 (2)
Sn–Cl(1′)	3.5607 (7)
C–C Distances in the Cyclopropenone Ring	
C(3)–C(4)	1.397 (3)
C(3)–C(5)	1.402 (3)
C(4)–C(5)	1.376 (3)
Other Distances	
O–C(3)	1.239 (3)
C(4)–C(6)	1.450 (3)
C(5)–C(12)	1.436 (3)

[a] Estimated standard deviations in parentheses.

Table VI. Intramolecular Angles (Deg) in $[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$[a]

Cl(1)–Sn–Cl(2)	91.94 (2)
Cl(1)–Sn–O	172.32 (5)
Cl(1)–Sn–C(1)	99.81 (8)
Cl(1)–Sn–C(2)	93.16 (6)
Cl(2)–Sn–O	80.92 (5)
Cl(2)–Sn–C(1)	104.43 (8)
Cl(2)–Sn–C(2)	110.46 (8)
O–Sn–C(1)	84.82 (9)
O–Sn–C(2)	86.75 (9)
C(1)–Sn–C(2)	142.2 (1)
Sn–O–C(3)	132.7 (2)
C(4)–C(3)–C(5)	58.9 (2)
C(3)–C(4)–C(5)	60.7 (2)
C(3)–C(5)–C(4)	60.4 (2)
Cl(1′)–Sn–Cl(1)	77.26 (2)
Cl(1′)–Sn–Cl(2)	166.10 (2)
Cl(1′)–Sn–O	110.23 (5)
Cl(1′)–Sn–C(1)	69.45 (7)
Cl(1′)–Sn–C(2)	79.25 (8)
Sn–Cl–Sn′	102.71 (2)

[a] Estimated standard deviations in parentheses.

For the cyclopropenone system sufficient structural data are now available to measure the onset of the effect of the utilization of the carbonyl oxygen atom lone pairs of electrons on the C═O distance and the ring dimensions. The four points of comparison are the anhydrous diphenylcyclopropenone, the two differently hydrogen-bonded molecules in its monohydrate, which are bound by one and two waters, and our title organotin complex. The structural data should reflect a change from form I to form II with involvement of the oxygen lone pairs in donation, especially a lengthening of the carbonyl C═O and ring C═C distances and a shortening of the ring C—C distance; i.e., the ring should take on a more symmetrical form. The salient ligand parameters for the family of known structures are listed in Table X.

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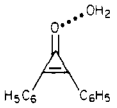
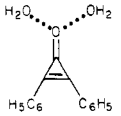
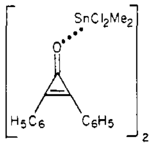
Table X. Comparison of Molecular Structure Data for Cyclopropenones

compound		d(C=O), Å	d(C=C), Å	$d(C-C)_{av}$, Å	$d(C-C_6H_5)_{av}$, Å	∠C–C(O)–C, deg	Δ[d(C–C) – d(C=C)], Å
acetone	mw[a]	1.212		1.519		116.2	
	ed[b]	1.211		1.517			
cyclopropanone	mw[c]	1.191		1.475		64.6	
cyclopropene	ed[d]		1.28	1.52		49.9	0.24
	ed[e]		1.304	1.519		g	0.215
	mw[f]		1.300	1.515		g	0.215
cyclopropenone	mw[h]	1.212	1.302	1.412		54.9[i]	0.110
2,3-diphenylcyclopropenone	X-ray[j,k]	1.225 (6)	1.348 (7)	1.416 (7)	1.447 (7)	56.9 (4)	0.068
2,3-bis(4-chlorophenyl)-cyclopropenone	X-ray[l,m]	1.30	1.48	1.42	1.37	62.2	0.06
2,3-diphenylcyclopropenethione	X-ray[n]	1.630 (C=S)	1.338	1.403	1.440	57.0	0.065
	X-ray[k,o]	1.238 (9)	1.365 (12)	1.405 (11)	1.439 (11)	58.1 (5)	0.040
	X-ray[p]	1.222	1.356	1.409	1.451	57.5	0.053
	X-ray[k,q]	1.245 (10)	1.376 (10)	1.389 (11)	1.441 (10)	59.4 (5)	0.013
	X-ray[r]	1.230	1.352	1.410	1.454	57.5	0.58
	X-ray[s]	1.239 (3)	1.376 (3)	1.400 (3)	1.443 (3)	58.9 (2)	0.024

[a] Reference 30. [b] Reference 31. [c] Reference 32. [d] Reference 33. [e] Reference 34. [f] Reference 35. [g] Not given. [h] Reference 6. [i] Not given in ref 6; calculated by assuming the two other interior angles are equal. [j] Reference 5. [k] Calculated by us from the final atomic coordinates (*H. Shimanouchi, private communication, 1981*). [l] Reference 9. [m] *Criticized in ref 8 as listing erroneous dimensions.* [n] Reference 36. [o] There are two crystallographically independent formula units per asymmetric unit, one hydrogen bonded to one water molecule, whose dimensions are listed here. [p] Reference 7. [q] There are two crystallographically independent formula units per asymmetric unit, one hydrogen bonded to two water molecules. [r] Reference 8. [s] This work.

Inspection of these data reveals a trend in the intraring and C═O distances on involvement of the oxygen in hydrogen bonding and donation. The anhydrous free ligand shows generally the shortest double bond d(C═O) and d(C═C) distances and the longest single bond d(C—C),[5] with all three distances in the gas-phase parent cyclopropenone somewhat smaller.[9] The carbonyl d(C═O) generally increases on forming one and then two hydrogen bonds with our tin complex resembling the doubly hydrogen-bonded molecule in the hydrate. Likewise, the d(C═C) distance increases in length generally in progressing to the tin complex, while the average d(C—C) distance decreases. Attempts at exact comparison are confused by the disagreement between the two X-ray structures for the monohydrate; for example, the data in ref 8 do not show the changes in the expected direction in going from the singly to the doubly hydrogen-bonded molecules observed in ref 5. However, it is apparent that complexation to tin works the largest lengthening effect on the carbonyl and ring double bonds and in symmetrizing the ring shape. The difference between the single- and double-bond distances in the ring, Δ[d(C—C) – d(C═C)], decreases from 0.068 in the free ligand to 0.024 Å in the tin complex, and the intraring angle ∠C—C(O)—C increases from 56.9° to 58.9 (2)°. The slight shortening of the connections to the phenyl groups is also in the direction expected from a larger contribution of form II.

The intraring internuclear distances would not be expected to be precisely equal, even in the ideal structure II, because of the basic asymmetry of the ring. In addition, the $d(C-C)_{av}$ in triphenylcyclopropenium perchlorate[37] of 1.373 Å, cited frequently as the standard length of a completely delocalized cyclopropenium connection,[1] is not very different from the 1.392-Å average of the three intraring carbon–carbon distances in our tin complex. It is thus likely on this evidence that the ligand trapped as the tin adduct is close to that represented by structure II, although something of the shorter, π character is retained in the C(4)–C(5) distance [1.376 (3) Å], and the angles at these carbon atoms are also relatively more open [60.7 (2)° and 60.4 (2)°, respectively] compared with the angle at C(3) [58.9 (2)°].

The magnitude of the O→Sn distance is another test of whether structure II has been trapped in the title complex, since this linkage should be expected to be more ester-like in the C—O—Sn linkage from form II than in the donor C═O→Sn linkage from form I. The former d(Sn–O) should be the shorter of the two. We are aware of ten structures in which carbonyl groups are linked to tin(IV), six inorganic and four organotin, of which eight are part of chelated systems.[19] Seven different ligand systems have been studied, the *N*-benzoyl-*N*-phenyl-*O*-hydroxylamino,[38,39] oxalato,[40] acac [1,3-diphenylpropane-1,3-dionato (dibenzoylmethano)[41] and 2,4-pentanedionato[42]], acetoacetic ethyl ester,[43] triphenylphosphoranylideneacetono,[44] salicylaldehydo,[20] and tropolonato.[45] The last named ligand is related to our cyclopropenone system

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Table XI. Comparison of Molecular Structure Data for Systems Containing Carbonyl Oxygen to Tin(IV) Coordination

compound	*d*(C=O → Sn), Å		C=O → Sn, deg
(1,3-diphenylpropane-1,3-dionato)triphenyltin[a]	1.290	2.094	135.3
	1.260	2.276	132.1
bis(2,4-pentanedionato)-dichlorotin[b]	1.290	2.051	124.5
	1.275	2.064	125.0
bis(ethyl 3-oxobutanato)-dichlorotin[c]	1.322	2.066	216.5
	1.293	2.101	123.1
(*N*-benzoyl-*N*-phenyl-*O*-hydroxylamine)triphenyltin[d]	1.265	2.308	112.1
bis(*N*-benzoyl-*N*-phenyl-*O*-hydroxylamine)dichlorotin[e]	1.30	2.180	111
$Sn(C_7H_5O_2)_3Cl{\cdot}CHCl_3$[f]	1.290[g]	2.103[g]	117.6[g]
	1.284[g]	2.156[g]	116.5[g]
$Sn(C_7H_5O_2)_3OH$[f]	1.299[g]	2.110[g]	118.6[g]
	1.271[g]	2.183[g]	117.2[g]
$(CH_3)_3SnCl$(triphenyl-phosphoranylideneacetone)[h]	1.268	2.332	134.3
$(CH_3)_2SnCl_2{\cdot}$salicylaldehyde[i]	1.23	2.680	134 (1)[j]
$[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$[k]	1.239 (3)	2.380 (2)	132.7 (2)

[a] Reference 38. [b] Reference 42. [c] Reference 43. [d] Reference 38. [e] Reference 39. [f] Reference 45. [g] Averaged for the three ligands in the molecule. [h] Reference 44. [i] Reference 20. [j] Reference 46. [k] This work.

in the ability of its ring system to delocalize positive charge, but only the tris inorganic complexes have been studied in which the tin atom is seven-coordinated.[45] The first named[38,39] and the $(C_6H_5)_3P{-}\ddot{C}H{-}C(O)CH_3$[44] ligands also enjoy enhanced basicity because of the lone pair of electrons on the atom α to the carbonyl group, but the former forms chelates as do the acac,[41,42] β-keto ester, and oxalato[40] derivatives. Selected data for these systems are listed in Table XI.

The most direct available comparison to our complex is the 1:1 adduct of dimethyltin(IV) dichloride with salicylaldehyde, whose structure we can now reinterpret. The ligand does not chelate the tin atom but is instead bonded *inter*molecularly as well through a bridging phenolic oxygen atom rather than through chlorine as in the title compound. The aldehydic donor oxygen in this ligand is also engaged in hydrogen bonding with its ortho phenolic neighbor and is thus trifurcatedly coordinated. Examination of the unit cell reveals a close contact at 3.366 Å to the phenolic oxygen (also thus trifurcated) of an adjacent molecule.[46] The system is thus better described as an associated solid of six-coordinated tin moieties.

The data in Table XI allow systematics to be derived in which the longest C=O distances are found contiguous to the shortest O→Sn distances and vice versa, as in the dichlorotin(IV) derivatives of the β-keto ester, where the keto *d*(C=O) = 1.322 Å is paired with a *d*(O→Sn) = 2.066 Å,[43] or with acac, where the *d*(C=O) = 1.290 Å is paired with a *d*(O→Sn) = 2.051 Å,[42] or with *N*-benzoyl-*N*-phenyl-*O*-hydroxylamine, where the *d*(C=O) = 1.30 Å is paired with a *d*(O→Sn) = 2.180 Å.[39,47] These examples are undoubtedly closest to the ester system C–O–Sn. The dimethyltin(IV) dichloride salicylaldehyde complex with the shortest distance *d*(C=O) = 1.23 Å and the longest distance *d*(O→Sn) = 2.680 Å,[20] on the other hand, represents the situation closest to the carbonyl donor system C=O→Sn currently available from structural studies. In this logic the diphenylcyclopropenone ligand in our tin complex with *d*(C=O) = 1.239 (3) and *d*(O→Sn) = 2.380 (2) Å behaves very much as a conventional carbonyl donor system of structure I and not as the ester system expected from structure II.

In our structure the carbonyl group vector makes a C=O→Sn angle of 132.7 (2)° at oxygen, while the corresponding angle in the salicylaldehyde analogue is 134 (1)°.[46] The only other nonchelated example for comparison is the phosphoranylacetone complex with trimethyltin(IV) chloride, for which the angle is 134.4°.[44] Thus the hybridization at the oxygen atom may be described as somewhat opened (more s character) from sp^2 (two lone pairs plus the C–O bonding pair) with the third lone pair in a p orbital available for π interaction with the aromatic system of the cyclopropenone ring, as in canonical form I. If this π interaction were important, then the planes of the C=O→Sn system and the ligand ring should be coincident, since the electron-donating, lone-pair orbital would lie in the ligand ring plane. The angle between these planes is only 11.7 (2)° in the title complex, and this result could be interpreted in terms of a donor carbonyl unit. Forcing the two planes into exact coincidence would maximize the steric interference of one of the ligand phenyl rings attachments, which are also in the ligand ring plane (see below) with the other substituents on the tin atom. As it is the ortho hydrogen on one of the phenyl rings makes a short contact with the bridging chlorine atom (see below).

The distortion from perfect octahedral geometry at tin is seen in the trans angle made by the Cl–Sn–O atoms [172.32 (5)°] vs. 177.44° for the salicylaldehyde structure[20,46]). The distortion can also be seen in the ∠C–Sn–C in the *trans*-dimethyltin system [142.2 (1)°] (vs. 131.4° in the salicylaldehyde complex[20,46]). The angle in solid dimethyltin(IV) dichloride itself of 124° is attributed to weak association in this phase.[48] In all three dimethyltin(IV) dichloride analogues a bridging atom of an adjacent molecule binds at a point between the two carbon–tin vectors, enhancing the opening of the angles. Some incipient angle opening derives from the unequal distribution of s character in the girdle of the molecule with the tin atom exerting a bonding orbital with much more p character toward the more electronegative chlorine atoms, leaving the methyl groups held by orbitals with relatively high s orbital hybridization, with the concomitant angle opening. The tin atom lies 0.0266 Å out of the plane formed by its two methyl groups, its terminally bonded chlorine [Cl(2)] and the chlorine atom bridged to it [Cl(1′)], in the direction of the Sn–Cl(1) vector. The shortest bond is made to the terminal chlorine [*d*(Sn–Cl(2)) = 2.3713 (6)] and the next shortest to the chlorine atom that bridges [*d*(Sn–Cl(1)) = 2.4745 (7) Å]. The chlorine atoms in the salicylaldehyde analogue that do not engage in bridging are found at 2.347 and 2.403 Å.[20,46]

The central Sn_2Cl_2 ring is bent through the torsional angles Sn–Cl(1)–Sn′–Cl(1′) and Cl–Sn–Cl(1′)–Sn′, which are coincidentally identical at 2.25 (3)°. The dihedral angle between the planes defined by the Sn–Cl–Sn′ and Sn–Cl(1′)–Sn′ atoms is 3.01 (2)° and that between Cl(1)–Sn–Cl(1′) and Cl(1)–Sn–Cl(1′) is 2.44°. This gives a ring in which the interior distances are *d*(Sn- - -Sn′) = 4.7623 (2) Å and *d*(Cl- - -Cl(1′)) = 3.8621 (10) Å. The sum of the interior angles is 359.94°.

The bridging chlorine, Cl(1′), makes a short intradimer contact with an orthocarbon of one of the ligand phenyls and its attached hydrogen, *d*[Cl(1′)--H(7)] = 2.79 (3) Å. Another close contact occurs between this chlorine and a hydrogen on one of the methyl groups, *d*[Cl(1′)--H(1)] = 2.93 (3) Å.

The ligand is relatively flat, occupying the least-square planes listed in Table IX. The phenyl rings are tilted at 2.5° and 8.4° from the plane of the cyclopropene.

We have recently solved the structure of the 1:1 adduct of dimethyltin(IV) dichloride with 2,6-dimethylpyridine (2,6-lutidine) *N*-oxide, which also forms dimers in the solid through bridging chlorine atoms.[24,49]

Acknowledgment. Our work is supported by the Office of Naval Research and the National Science Foundation through Grant CHE-78-26548 (J.J.Z.) and the National Cancer Institute, DHEW, through Grant CA-17562 (D.v.d.H.). We thank the

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University of Oklahoma for providing computer time.

Registry No. $[(CH_3)_2SnCl_2\cdot O{=}CC_2(C_6H_5)_2]_2$, 82639-34-7.

Supplementary Material Available: A listing of observed and calculated structure amplitudes, the thermal parameters (Table IV), hydrogen parameters (Table VII), the carbon–carbon and carbon–hydrogen distances and the carbon–carbon–carbon angles in the phenyl rings (Table VIII), and least-squares planes (Table IX) (24 pages). Ordering information is given on any current masthead page.

Polarized X-ray Absorption Spectra of Oriented Plastocyanin Single Crystals. Investigation of Methionine–Copper Coordination

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Abstract: Polarized X-ray absorption spectra have been recorded for oriented single crystals of the "blue" copper protein plastocyanin from *Populus nigra* var. *italica*. From the crystal structure of plastocyanin, it is known that the sulfur atom of a methionine residue is located 2.90 Å from the Cu atom. In prior analyses of the extended X-ray absorption fine-structure (EXAFS) spectra of plastocyanin and other blue copper proteins in solution, the contribution of this sulfur to the EXAFS appeared to be weak or absent. The symmetry properties of plastocyanin crystals have now enabled us to record X-ray absorption spectra of plastocyanin in two orientations in which all of the Cu–S(Met) bonds are either parallel to or perpendicular to the polarization vector of the incident synchrotron X-radiation. In the first of these orientations, the ability to detect the Cu–S(Met) EXAFS should be significantly enhanced. Comparison of spectra from the two orientations confirms that the methionine sulfur makes a negligible contribution to the EXAFS. Possible reasons for this noncontribution, and their significance for EXAFS structure determinations, are discussed. In addition, the structure of the X-ray absorption edge of plastocyanin crystals is found to be strongly orientation dependent.

The so-called "type 1" or "blue" copper proteins have an extremely intense (ca. 3000–5000 M^{-1} cm^{-1}) absorption band near 600 nm, a very small hyperfine splitting in the $g_\parallel$ region of the EPR spectrum, and an unusually high reduction potential. A great deal of effort has been devoted to developing a detailed structural interpretation of these unique features. The molecular structures of two blue copper proteins, plastocyanin from poplar leaves (*Populus nigra* var. *italica*) and azurin from *Pseudomonas aeruginosa*, are now known from X-ray crystallographic studies.[1,2] In the oxidized [Cu(II)] state, both proteins contain a copper atom coordinated to the nitrogen atoms of two histidine residues, a cysteine sulfur, and a methionine sulfur. A refinement of the plastocyanin structure at 1.6-Å resolution has shown that the metal–ligand distances are Cu–N(His) = 2.04 and 2.10 Å, Cu–S(Cys) = 2.13 Å, and Cu–S(Met) = 2.90 Å, with esd's of about 0.05 Å.[3,4] Although the unique features of blue copper protein sites have been substantially rationalized in terms of the X-ray structural results, the significance of the extremely long Cu–S(Met) bond in relation to the properties of plastocyanin remains a subject for speculation and study.[4,5] Single-crystal electronic absorption spectra and EPR spectra have shown that the methionine sulfur has at most a very small effect on the ligand field at the copper atom.[6]

Previous extended X-ray absorption fine-structure (EXAFS) analysis of solutions of plastocyanin from French beans (*Phaseolus vulgaris*) yielded results in substantial agreement with the crystallographic distances from the copper to the three close ligands (2 N(His) at 1.97 Å and an S(Cys) at 2.11 Å).[7] However, as in similar experiments on solutions of azurin,[8] the presence of the more distant S(Met) ligand could not be unequivocally demonstrated from the EXAFS analysis. In order to improve our understanding of the contribution of the S(Met) ligand to the Cu EXAFS, we have undertaken an X-ray absorption spectroscopic study of plastocyanin single crystals. To the best of our knowledge, this is the first such study of a protein in the crystalline state.

Plastocyanin crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell. These four symmetry-related molecules have their Cu–S(Met) bonds aligned approximately parallel to the crystallographic *c* axis. The three other copper–ligand bonds in each molecule lie roughly normal to the *c* axis as a result of the distorted tetrahedral (or elongated C_{3v}) coordination geometry of the Cu atoms. These symmetry properties are crucial to the experiments described herein.

The amplitude of the EXAFS from a given scatterer is proportional to the square of the cosine of the angle between the X-ray

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