# The Crystal Structure of Distannous Ethylenediaminetetraacetate Dihydrate

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The crystal and molecular structure of distannous ethylenediaminetetraacetate dihydrate, $C_{10}H_{16}N_2O_{10}Sn_2$, has been determined by a single-crystal, three-dimensional X-ray diffraction study. The compound crystallizes in the noncentrosymmetric space group $P1$ with one formula weight in each triclinic unit cell of dimensions $a = 7.732 \pm 0.003$, $b = 8.110 \pm 0.003$, $c = 6.599 \pm 0.003$ Å, $\alpha = 94.15 \pm 0.05$, $\beta = 87.80 \pm 0.02$, and $\gamma = 107.97 \pm 0.02°$. The calculated and observed densities are 2.376 and 2.319 g cm$^{-3}$, respectively. The intensity data were obtained on a Picker automatic diffractometer (Mo $K\alpha$ radiation, $\lambda$ 0.71069 Å), and the structure was solved by the heavy-atom method. Least-squares refinement assuming anisotropic thermal motion converged to a discrepancy index $R = 4.7\%$ for 1649 reflections above background. Hydrogens were not located. The different environments found both for the tin atoms and the water molecules show that, in the solid, the complex may be represented by the formula $Sn^{II}[Sn^{II}Y \cdot H_2O] \cdot H_2O$ ($H_4Y$ = ethylenediaminetetraacetic acid). The geometry of the inner coordination sphere around tin in the hexadentate $\psi$ seven-coordinate SnY moiety, which exhibits approximate $C_2$ symmetry, is a distorted pentagonal bipyramid where the ethylenediamine nitrogens and the tin lone electron pair occupy equatorial positions. The remaining sites are taken by an oxygen from each of the four carboxylate substituents. Each SnY unit is bonded to four Sn(II) atoms of the second type *via* carboxylate oxygens. $\psi$ octacoordination around this Sn atom is completed through weaker bonds with three additional oxygen atoms; the lone electron pair on tin occupies the eighth coordination site. The configuration around this tin atom can be viewed as built up from two interlocked tetrahedra, elongated and flattened, respectively. The two water molecules, which are hydrogen bonded to each other, are held in the lattice in different ways: W(1) is linked to two adjacent SnY moieties through hydrogen bonds with two carboxylate oxygens, but W(2) is only hydrogen bonded to one SnY unit *via* one oxygen atom.

## Introduction

Hoard and coworkers have described the structural systematics of crystalline complexes of ethylenediaminetetraacetic acid (EDTA, $H_4Y$) with many different cations.[1] Octahedral configurations are formed by the pentadentate $Ni(OH_2)H_2Y$ and $Cu(OH_2)H_2Y$ chelates[2] and the hexadentate isomorphous $CoY^-$, $CrY^-$, and $AlY^-$ ions.[3] The chelating versatility of $Y^{4-}$ is also clearly demonstrated in the hexadentate seven-coordinate $Mn(OH_2)Y^{2-}$[4] and $Fe(OH_2)Y^-$[5] and the hexadentate ten-coordinate $La(OH_2)_3Y^-$[6] aquo complexes.

Complexes of EDTA with divalent[7-9] and tetravalent[10] ions of group IV metals have been reported by several workers and Langer has studied the physical and chemical properties of several tin(II) chelates in the solid state[11] and in aqueous solution,[12] including $Na_2Sn^{II}Y \cdot 2H_2O$, $CaSn^{II}Y \cdot 4H_2O$, and $Sn^{II}_2Y \cdot 2H_2O$. On the basis of spectral differences between $Na_2Sn^{II}Y \cdot 2H_2O$ and $Sn^{II}_2Y \cdot 2H_2O$ Langer proposed a binuclear structure $[H_2O-SnYSn-OH_2]$ for the latter material in preference to a salt of the type $Sn^{2+}[SnY]^{2-} \cdot 2H_2O$. In the infrared spectrum both water molecules in the crystalline complex appear to be identical, but the available evidence could not unambiguously assign their functional role. The low frequencies for carbonyl stretching were believed to arise either from hydrogen bonding between water and carbonyl groups or alter-

natively by inter- or intramolecular participation of both oxygen atoms of a carboxylate group in coordination to the metal.

We have undertaken a complete three-dimensional X-ray analysis of the $Sn^{II}_2Y \cdot 2H_2O$ complex to resolve the question of its structure and to determine directly the functional role of the water molecules. Our study clearly establishes the compound as an asymmetric polynuclear complex in the solid. All eight carboxylate oxygens are bonded to at least one tin atom. The water molecules are held in the crystal by hydrogen bonds to carboxylate oxygens but are not directly bonded to tin.

The presence of a lone pair of electrons on the central atom provides an additional motive for studying the structural systematics of Sn(II) salts[13-17] and complexes.[18] A number of structures have been studied by X-ray diffraction methods[13-18] but we believe our results are the first descriptions of $\psi$ seven- and $\psi$ eight-coordination of Sn(II) in the solid state.

## Experimental Section

A sample of distannous ethylenediaminetetraacetate dihydrate, $Sn^{II}_2Y \cdot 2H_2O$, was kindly supplied by H. G. Langer. The colorless crystals are stable both to the atmosphere and to X radiation. The reciprocal lattice symmetry ($C_i^1$; $\bar{1}$) observed from preliminary Weissenberg and precession photographs indicated that the crystals belong to the triclinic system. The crystals are well-formed parallelepipeds with large and distinct (100), (010), and (001) faces.

A crystal of dimensions $0.17 \times 0.08 \times 0.10$ mm (in the $a^*$, $b^*$, and $c^*$ directions) was sealed in a 0.2-mm thin-walled glass capillary. This crystal was carefully centered on a Picker four-circle automatic diffractometer and aligned with its $a$ axis collinear with $\phi$. Accurate lattice constants were calculated by least-squares refinement of the goniostat setting angles of 14 reflections (Mo $K\alpha$ radiation, $\lambda$ 0.71069 Å). The cell parameters, $a = 7.732 \pm 0.003$, $b = 8.110 \pm 0.003$, $c = 6.599 \pm 0.003$ Å, $\alpha = 94.15 \pm$

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(9) D. T. Sawyer and P. J. Paulsen, *J. Amer. Chem. Soc.*, **81**, 816 (1959).
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TABLE I
FINAL STRUCTURE PARAMETERS[a] AND ESTIMATED STANDARD DEVIATIONS[b]

| Atom | $x$ | $y$ | $z$ | $10^4\beta_{11}$ | $10^4\beta_{22}$ | $10^4\beta_{33}$ | $10^4\beta_{12}$ | $10^4\beta_{13}$ | $10^4\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Sn(1) | 0.0 | 0.0 | 0.0 | 101 (4) | 122 (4) | 119 (4) | 30 (3) | 20 (3) | 27 (3) |
| Sn(2) | 0.5123 (2) | 0.3346 (2) | 0.7699 (2) | 103 (4) | 109 (3) | 110 (4) | 30 (3) | −15 (3) | −7 (3) |
| O(1) | 0.266 (1) | 0.030 (1) | 0.857 (2) | 111 (21) | 104 (20) | 110 (25) | 19 (16) | −2 (19) | 3 (18) |
| O(2) | 0.266 (2) | −0.252 (2) | 0.837 (2) | 169 (28) | 149 (25) | 229 (37) | 39 (21) | −7 (25) | 55 (24) |
| O(3) | 0.374 (2) | 0.372 (1) | 0.483 (2) | 139 (23) | 111 (20) | 161 (29) | 46 (18) | −21 (21) | 30 (20) |
| O(4) | 0.200 (2) | 0.250 (2) | 0.230 (2) | 159 (28) | 169 (27) | 226 (40) | 95 (22) | −38 (26) | −2 (25) |
| O(1*) | 0.730 (3) | 0.654 (2) | 0.836 (2) | 257 (43) | 135 (25) | 152 (48) | −35 (26) | 102 (35) | −37 (31) |
| O(2*) | 0.907 (2) | 0.878 (2) | 0.684 (2) | 124 (23) | 126 (22) | 148 (29) | 9 (18) | −32 (20) | −7 (20) |
| O(3*) | 0.747 (2) | 0.209 (1) | 0.862 (2) | 125 (21) | 147 (30) | 94 (28) | 45 (22) | −8 (19) | −4 (22) |
| O(4*) | 1.041 (2) | 0.228 (1) | 0.835 (2) | 117 (22) | 110 (20) | 186 (31) | 46 (17) | −12 (21) | 36 (20) |
| N | 0.486 (2) | 0.085 (1) | 0.530 (2) | 106 (24) | 72 (20) | 89 (27) | 47 (18) | 19 (20) | −23 (19) |
| N* | 0.776 (2) | 0.422 (2) | 0.540 (2) | 81 (23) | 95 (21) | 103 (29) | 6 (18) | −2 (21) | 42 (20) |
| C(1) | 0.661 (2) | 0.116 (2) | 0.401 (2) | 99 (30) | 140 (30) | 91 (33) | 34 (25) | 54 (25) | −37 (25) |
| C(2) | 0.453 (2) | −0.081 (2) | 0.628 (2) | 185 (37) | 75 (24) | 104 (34) | 64 (25) | 29 (29) | 4 (23) |
| C(3) | 0.302 (2) | −0.108 (2) | 0.787 (2) | 100 (28) | 82 (25) | 125 (35) | −5 (21) | −35 (25) | 15 (24) |
| C(4) | 0.326 (3) | 0.071 (2) | 0.393 (2) | 195 (44) | 93 (28) | 80 (37) | 2 (27) | −35 (30) | 19 (25) |
| C(5) | 0.302 (2) | 0.241 (2) | 0.361 (3) | 53 (26) | 124 (30) | 225 (49) | 45 (22) | 29 (28) | 58 (30) |
| C(1*) | 0.735 (2) | 0.304 (2) | 0.352 (2) | 104 (29) | 134 (29) | 60 (30) | 3 (23) | 17 (23) | 11 (24) |
| C(2*) | 0.808 (2) | 0.610 (2) | 0.492 (3) | 138 (33) | 52 (22) | 222 (46) | 20 (22) | −34 (31) | 66 (26) |
| C(3*) | 0.818 (2) | 0.722 (2) | 0.688 (2) | 122 (33) | 66 (26) | 253 (23) | 31 (23) | −21 (33) | 26 (29) |
| C(4*) | 0.940 (2) | 0.409 (2) | 0.635 (2) | 99 (29) | 93 (26) | 134 (37) | 28 (22) | −2 (26) | 14 (25) |
| C(5*) | 0.900 (2) | 0.270 (2) | 0.788 (2) | 126 (32) | 115 (28) | 123 (36) | 35 (24) | −49 (27) | 0 (26) |
| W(1) | 0.174 (3) | 0.591 (3) | 0.207 (3) | 520 (68) | 301 (45) | 309 (54) | 224 (46) | 169 (49) | 123 (41) |
| W(2) | 0.551 (3) | 0.746 (3) | 0.162 (4) | 394 (67) | 435 (68) | 544 (89) | 66 (53) | 76 (62) | −37 (62) |

[a] The anisotropic thermal parameters are in the from $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$. [b] Estimated standard deviations are given in parentheses.

0.05, $\beta = 87.80 \pm 0.02$, and $\gamma = 107.97 \pm 0.02°$, give a unit cell volume of 392.5 Å$^3$ and a calculated density of 2.376 g cm$^{-3}$ for $C_{10}H_{16}N_2O_{10}Sn_2$ with $Z = 1$. The observed density measured by flotation in a mixture of methylene bromide and ethylene bromide at 23° is 2.319 ± 0.005 g cm$^{-3}$. The Delaunay reduced cell[19] has dimensions $a' = 7.732$, $b' = 6.599$, $c' = 10.078$ Å, $\alpha' = 126° 38'$, $\beta' = 102° 54'$, and $\gamma' = 92° 12'$ and can be obtained by the transformation matrix

$$S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 1 \end{pmatrix}$$

Intensity data were collected using the $\theta$–$2\theta$ scan mode of the diffractometer with Zr-filtered molybdenum radiation. The takeoff angle of the tube was 2°, and a detector aperture 6.0 mm square was placed 30 cm from the crystal. Angles ranging between 2.0 and 2.4° of $2\theta$ were scanned at a speed of 2°/min, and two stationary-crystal, stationary-counter background counts of 15 sec were taken at each end of the scan. The reciprocal lattice was recorded out to the limit of the Cu K$\alpha$ sphere (sin $\theta$ = 0.461) and a total of 1799 reflections were measured. The (111) reflection, monitored every 50 measurements, showed good stability. A standard deviation estimated from counting statistics according to the formula

$$\sigma(I) = [(0.02I)^2 + N_0 + k^2 N_b]^{1/2}$$

was assigned to the net intensity $I = N_0 - kN_b$ in order to establish the weights $w = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, where the quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized. Here $N_0$ is the gross count, $N_b$ is the background count, $k$ is the ratio of scan time to background time, and the $F^2$ are the intensities corrected for Lorentz and polarization effects. The 150 reflections for which either $I < 0$ or $\sigma(I)/I > 0.5$ were denoted absent and were omitted from the structure analysis. The linear absorption coefficient $\mu$ for Mo K$\alpha$ radiation is 32.40 cm$^{-1}$; no absorption corrections were made. Transmission factors were estimated to range from 0.576 to 0.772.

## Solution and Refinement of the Structure

An absolute scale factor and an overall temperature factor were computed by Wilson's method. The relative positions of the tin atoms in the triclinic cell were determined from a normal-sharpened three-dimensional

Patterson function.[20] Evaluation of the number and the intensities of the tin–light atom vectors in this map indicated the noncentrosymmetric space group P1, which was confirmed by the subsequent structure analysis. Least-squares refinement[21] of the relative positions of the tin atoms gave a discrepancy index

$$R_1 = \frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|} = 0.167$$

A three-dimensional Fourier synthesis, phased on both tin atoms, showed the symmetry of space group P$\bar{1}$. From the 44 highest peaks in this map, several chemically reasonable molecular fragments were selected and included in the model. Care was exercised that no atoms related by the false center of symmetry were included. It soon became apparent, however, that addition to the phasing model of even a considerable number of light atoms would not assist in the resolution of the ambiguity. Finally, an entire EDTA unit consisting of the 20 highest peaks in the map was picked out from its image. Least-squares refinement[21] of the positional parameters and isotropic temperature factors of these atoms reduced $R_1$ from an initial value of 0.104 to 0.075. A difference Fourier[20] revealed pairs of positions for the water oxygens with unequal peak heights: W(2) weaker than W(1). Even now the false images were present with nearly identical intensities. Four peaks present in the first Fourier map, but not included in the model, had vanished. The correct member of each enantiomorphous pair of water molecules was selected by consideration of intra- and intermolecular contacts. This structure was later confirmed by direct phasing using the anomalous scattering of the tin atoms on a data set ob-

(19) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 530.

(20) Fourier calculations were performed on the IBM 1130 computer, using a program written by M. A. Neuman, and on the CDC 6600 computer, using program B-149 (Argonne National Laboratory), a version of Shoemaker, Sly, and van der Hende's ERFR-2 by J. Gvildys.

(21) FLS1130, by F. P. van Remoortere and F. P. Boer, is a full-matrix crystallographic least-squares program for the IBM 1130 computer. Core and disk storage limitations restrict it to 72 simultaneously varied parameters and 2000 reflections.
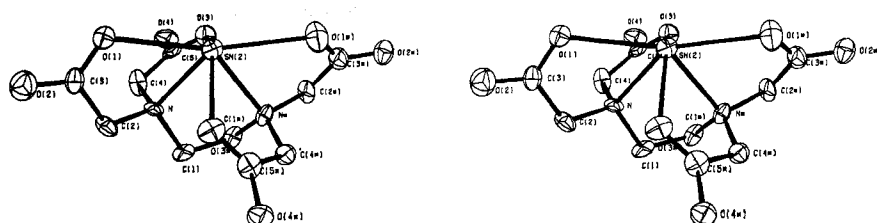
Figure 1.—Three-dimensional view of the SnY moiety in distannous ethylenediaminetetraacetate dihydrate showing ellipsoids of thermal motion.
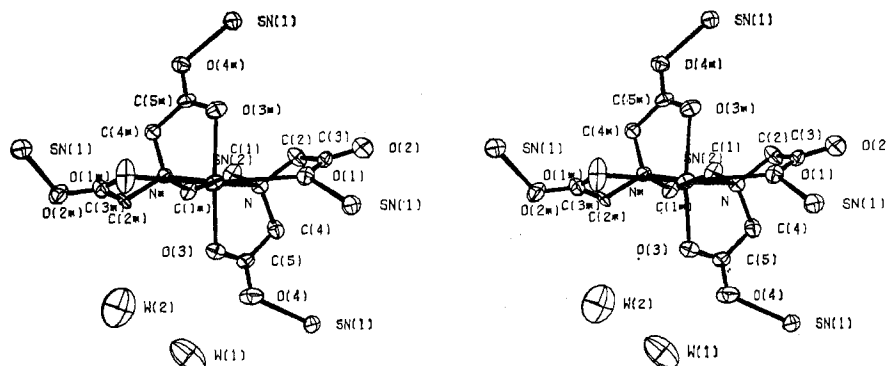


Figure 2.—Three-dimensional view of the structure of distannous ethylenediaminetetraacetate dihydrate along the approximate $C_2$ axis showing ellipsoids of thermal motion.
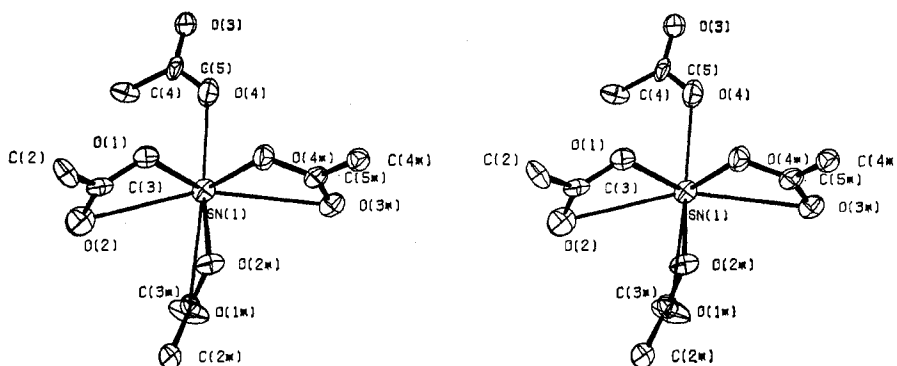


Figure 3.—Three-dimensional view of the coordination around Sn(1) in distannous ethylenediaminetetraacetate dihydrate.

tained with Cu K$\alpha$ radiation (see Appendix). Least-squares refinement[21] of the atomic positions and isotropic temperature factors on a small computer using blocks of 72 variables reduced $R_1$ to 0.064 and

$$R_2 = \left\{ \frac{\sum w[F_o - F_c]^2}{\sum w F_o{}^2} \right\}^{1/2}$$

to 0.073. A difference map[20] showed large residuals in the vicinity of the Sn atoms, but hydrogens could not be identified. Refinement was completed on a larger computer using full-matrix least squares[22] and assuming anisotropic temperature factors for Sn, O, N, and C. After the first cycle, in which $R_1$ was reduced to 0.049 and $R_2$ to 0.057, 24 strong low-order reflections, systematically less intense than their calculated values, were corrected for secondary extinction.[23] After introduction of these corrected values additional refinement[22] on all parameters converged in two more cycles to the final discrepancy indices of $R_1 = 0.047$ and $R_2 =$

0.053. In the final cycle the average shift in position parameters was $0.05\sigma$ with a maximum shift of $0.29\sigma$; the shifts in anisotropic thermal parameters were $0.08\sigma$ (av) and $0.90\sigma$ (max). A final difference map revealed some residual electron density as high as 0.94 e$^-$ Å$^{-3}$, and negative peaks |less| than 0.82 e$^-$ Å$^{-3}$ in the regions around the tin atoms. Throughout the analysis the scattering factors for neutral O, C, N, and Sn were used with no correction for dispersion.[24]

Atomic parameters and their estimated standard deviations are given in Table I. The directions of thermal motion may be inferred from Figures 1–4, in which the three-dimensional structure of the complex is shown using ellipsoids to represent the anisotropic thermal motion.[25] The root-mean-square components of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters, are compiled in Table II. Bond distances and bond angles, to-

(22) Anisotropic least-squares and structure factor calculations were performed using ANL-FLS-14E, J. Gvildys' version of Busing, Martin, and Levy's OR-FLS.

(23) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

(24) Atomic scattering factors for Sn, C, N, and O were taken from "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England 1962, p 201.

(25) ORTEP is a Fortran thermal ellipsoid plot program by C. K. Johnson, Oak Ridge National Laboratory.
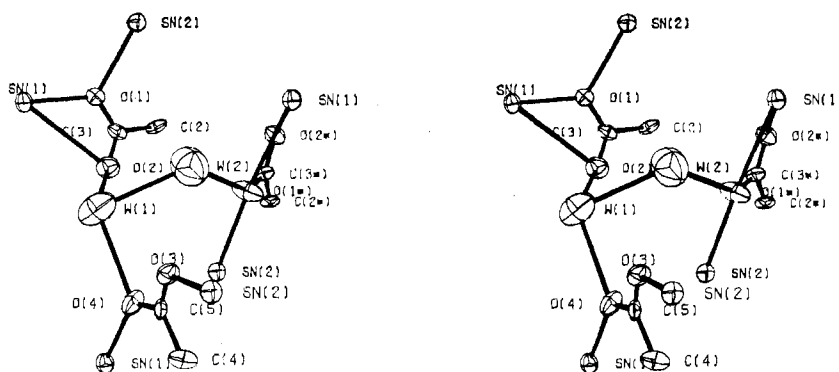
Figure 4.—Three-dimensional view of the environment of the water molecules in distannous ethylenediaminetetraacetate dihydrate.

TABLE II
ROOT-MEAN-SQUARE DISPLACEMENTS ALONG THE
PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS $(\text{Å})^{a,b}$

| Atom | Axis 1 | Axis 2 | Axis 3 |
|---|---|---|---|
| Sn(1) | 0.145 (3) | 0.177 (3) | 0.197 (3) |
| Sn(2) | 0.149 (3) | 0.172 (3) | 0.185 (3) |
| O(1) | 0.16 (2) | 0.17 (2) | 0.19 (2) |
| O(2) | 0.19 (2) | 0.21 (2) | 0.25 (2) |
| O(3) | 0.15 (2) | 0.19 (2) | 0.21 (2) |
| O(4) | 0.16 (2) | 0.22 (2) | 0.25 (2) |
| O(1*) | 0.14 (3) | 0.18 (2) | 0.34 (2) |
| O(2*) | 0.15 (2) | 0.20 (2) | 0.22 (2) |
| O(3*) | 0.14 (2) | 0.18 (2) | 0.21 (2) |
| O(4*) | 0.15 (2) | 0.19 (2) | 0.21 (2) |
| N | 0.09 (3) | 0.17 (2) | 0.18 (2) |
| N* | 0.12 (2) | 0.15 (2) | 0.20 (2) |
| C(1) | 0.07 (4) | 0.18 (2) | 0.23 (2) |
| C(2) | 0.13 (3) | 0.15 (3) | 0.23 (2) |
| C(3) | 0.13 (3) | 0.15 (2) | 0.21 (2) |
| C(4) | 0.12 (3) | 0.16 (3) | 0.25 (3) |
| C(5) | 0.11 (3) | 0.17 (2) | 0.24 (2) |
| C(1*) | 0.11 (3) | 0.16 (2) | 0.22 (2) |
| C(2*) | 0.09 (4) | 0.18 (2) | 0.24 (2) |
| C(3*) | 0.13 (3) | 0.18 (2) | 0.24 (2) |
| C(4*) | 0.16 (2) | 0.16 (2) | 0.18 (2) |
| C(5*) | 0.14 (3) | 0.19 (2) | 0.21 (2) |
| W(1) | 0.22 (3) | 0.26 (2) | 0.41 (3) |
| W(2) | 0.30 (3) | 0.33 (3) | 0.41 (3) |

$^a$ Ordered in increasing magnitude. $^b$ Estimated standard deviations as computed from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses.

gether with their standard deviations computed[26] from the variance–covariance matrix obtained in the final least-squares cycle, are listed in Tables III and IV, respectively. A table of observed and calculated structure factors is available to the interested reader.[27]

## Discussion

**A. Geometry of the SnY Moiety.**—One of the two unique tin atoms, Sn(2), is coordinated by the hexadentate ethylenediaminetetraacetate ligand Y in a distorted pentagonal-bipyramidal geometry where the two nitrogens and the tin lone pair occupy equatorial sites and the other four coordination sites are occupied by carboxylate oxygens (Figure 1). (The location of the unshared electrons appears probable from the coordination geometry but is, of course, experimentally unproven.) This substructure has approximately $C_2$ symmetry with the twofold axis passing through Sn(2),

(26) J. Gvildys' version (ANL Program Library B-115) of Busing, Martin, and Levy's Fortran function and error program, OR-FFE, was used.

(27) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036. Remit $3.00 for photocopy or $2.00 for microfiche.

TABLE III
INTERATOMIC DISTANCES $(\text{Å})^{a,b}$

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| (I) | $x$ | $y$ | $z$ |
| (II) | $x$ | $y$ | $z - 1$ |
| (III) | $x - 1$ | $y$ | $z - 1$ |
| (IV) | $x - 1$ | $y - 1$ | $z - 1$ |
| (V) | $x$ | $y + 1$ | $z - 1$ |
| (VI) | $x$ | $y$ | $z - 1$ |
| (VII) | $x$ | $y - 1$ | $z + 1$ |
| (VIII) | $x + 1$ | $y + 1$ | $z + 1$ |
| (IX) | $x + 1$ | $y$ | $z + 1$ |

Tin–Oxygen Distances

| | | | |
|---|---|---|---|
| Sn(1)–O(1) (II) | 2.18 (1) | Sn(1)–O(4*) (III) | 2.14 (1) |
| Sn(1)–O(2) (II) | 3.18 (1) | Sn(2)–O(1) | 2.70 (1) |
| Sn(1)–O(4) | 2.59 (1) | Sn(2)–O(3) | 2.29 (1) |
| Sn(1)–O(1*) (IV) | 3.10 (1) | Sn(2)–O(1*) | 2.64 (1) |
| Sn(1)–O(2*) (IV) | 2.30 (1) | Sn(2)–O(3*) | 2.45 (1) |
| Sn(1)–O(3*) (III) | 3.14 (1) | | |

Tin–Nitrogen Distances

| | | | |
|---|---|---|---|
| Sn(2)–N | 2.46 (1) | Sn(2)–N* | 2.45 (1) |

Carbon–Oxygen Bonds

| | | | |
|---|---|---|---|
| C(3)–O(1) | 1.29 (2) | C(3*)–O(1*) | 1.23 (2) |
| C(3)–O(2) | 1.20 (2) | C(3*)–O(2*) | 1.25 (2) |
| C(5)–O(3) | 1.28 (2) | C(5*)–O(3*) | 1.22 (2) |
| C(5)–O(4) | 1.22 (2) | C(5*)–O(4*) | 1.29 (2) |

Carbon–Nitrogen Bonds

| | | | |
|---|---|---|---|
| C(1)–N | 1.53 (2) | C(1*)–N* | 1.50 (2) |
| C(2)–N | 1.48 (2) | C(2*)–N* | 1.52 (2) |
| C(4)–N | 1.53 (2) | C(4*)–N* | 1.47 (2) |

Carbon–Carbon Bonds

| | | | |
|---|---|---|---|
| C(1)–C(1*) | 1.51 (2) | C(2*)–C(3*) | 1.53 (2) |
| C(2)–C(3) | 1.52 (2) | C(4*)–C(5*) | 1.52 (2) |
| C(4)–C(5) | 1.47 (2) | | |

Oxygen–Oxygen Distances (Hydrogen Bonds)

| | | | |
|---|---|---|---|
| W(1)–O(2) (V) | 2.79 (3) | W(1)–W(2) | 2.82 (3) |
| W(1)–O(4) | 2.85 (2) | W(2)–O(1*) (II) | 2.71 (3) |

$^a$ Estimated standard deviations calculated[26] from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses. $^b$ Atoms not followed by a Roman numeral refer to the basic unit cell (I).

the lone electron pair, and the midpoint of the C(1)–C(1*) ethylenediamine bond (atoms related by this diad are indicated by asterisks as, *e.g.*, C(1) and C(1*)). The SnY moiety in $Sn^{II}_2Y \cdot 2H_2O$ does not correspond to a sensibly discrete, doubly charged anion in view of its strong linking to Sn(1).

As Hoard and coworkers[4] have pointed out, a planar ethylenediamine ring {Sn, N, N*, C(1), C(1*)} with regular tetrahedral angles at carbon and nitrogen is not physically possible since metal–nitrogen distances below 1.65 Å would be required. (The observed Sn–N distances are 2.45 ± 0.01 and 2.46 ± 0.01 Å, respec-

Table IV
Interatomic Angles (deg)[a,b]

| Vertex | Atom 1 | Atom 2 | Angle | Vertex | Atom 1 | Atom 2 | Angle |
|---|---|---|---|---|---|---|---|
| Sn(1) | O(1) (II) | O(2) (II) | 43.9 (0.4) | Sn(1) | O(4) | O(1*) (IV) | 164.3 (0.4) |
| | O(1) (II) | O(4) | 79.6 (0.5) | | O(4) | O(2*) (IV) | 150.7 (0.5) |
| | O(1) (II) | O(1*) (IV) | 108.9 (0.5) | | O(4) | O(3*) (III) | 95.5 (0.4) |
| | O(1) (II) | O(2*) (IV) | 81.2 (0.4) | | O(4) | O(4*) (III) | 75.0 (0.5) |
| | O(1) (II) | O(3*) (III) | 121.2 (0.4) | | O(1*) (IV) | O(2*) (IV) | 44.9 (0.4) |
| | O(1) (II) | O(4*) (III) | 77.9 (0.4) | | O(1*) (IV) | O(3*) (III) | 91.1 (0.5) |
| | O(2) (II) | O(4) | 110.1 (0.4) | | O(1*) (IV) | O(4*) (III) | 119.0 (0.5) |
| | O(2) (II) | O(1*) (IV) | 71.4 (0.5) | | O(2*) (IV) | O(3*) (III) | 75.8 (0.4) |
| | O(2) (II) | O(2*) (IV) | 68.7 (0.5) | | O(2*) (IV) | O(4*) (III) | 79.4 (0.5) |
| | O(2) (II) | O(3*) (III) | 143.0 (0.3) | | O(3*) (III) | O(4*) (III) | 45.2 (0.4) |
| Sn(2) | N | O(1) | 62.4 (0.4) | Sn(2) | N* | O(1*) | 64.3 (0.5) |
| | N | O(3) | 70.9 (0.4) | | N* | O(3*) | 69.5 (0.4) |
| | N | O(1*) | 138.5 (0.4) | | N* | O(1) | 135.0 (0.4) |
| | N | O(3*) | 74.0 (0.4) | | N* | O(3) | 79.7 (0.5) |
| | O(1) | O(3) | 96.0 (0.4) | | O(1*) | O(3*) | 92.0 (0.6) |
| | O(1) | O(3*) | 87.1 (0.4) | | O(1*) | O(3) | 99.4 (0.5) |
| | N | N* | 74.2 (0.4) | | O(1) | O(1*) | 157.6 (0.4) |
| | O(3) | O(3*) | 138.2 (0.4) | | | | |
| O(1) | Sn(1) (VI) | Sn(2) | 125.3 (0.5) | O(1*) | Sn(1) (VIII) | Sn(2) | 167.9 (0.7) |
| | Sn(1) (VI) | C(3) | 117.7 (0.9) | | Sn(1) (VIII) | C(3*) | 73.9 (1.1) |
| | Sn(2) | C(3) | 116.4 (0.9) | | Sn(2) | C(3*) | 115.9 (1.1) |
| | | | | | Sn(1) (VIII) | W(2) (VI) | 76.6 (0.6) |
| | | | | | Sn(2) | W(2) (VI) | 98.0 (0.8) |
| | | | | | C(3*) | W(2) (VI) | 138.1 (0.6) |
| O(2) | Sn(1) (VI) | C(3) | 70.5 (1.0) | O(2*) | Sn(1) (VIII) | C(3*) | 112.5 (1.2) |
| | Sn(1) (VI) | W(1) (VII) | 90.7 (0.6) | | | | |
| | C(3) | W(1) (VII) | 133.7 (1.2) | | | | |
| O(3) | Sn(2) | C(5) | 119.9 (1.0) | O(3*) | Sn(2) | C(5*) | 117.1 (1.0) |
| | | | | | Sn(1) (IX) | Sn(2) | 171.4 (0.5) |
| | | | | | Sn(1) (IX) | C(5*) | 71.1 (0.9) |
| O(4) | Sn(1) | C(5) | 127.8 (1.1) | O(4*) | Sn(1) (IX) | C(5*) | 118.1 (1.0) |
| | Sn(1) | W(1) | 119.3 (0.7) | | | | |
| | C(5) | W(1) | 112.8 (1.2) | | | | |
| N | Sn(2) | C(1) | 109.6 (0.8) | N* | Sn(2) | C(1*) | 107.4 (0.8) |
| | Sn(2) | C(2) | 113.7 (0.8) | | Sn(2) | C(2*) | 108.6 (1.0) |
| | Sn(2) | C(4) | 106.8 (0.9) | | Sn(2) | C(4*) | 110.6 (0.9) |
| | C(1) | C(2) | 108.4 (1.2) | | C(1*) | C(2*) | 111.4 (0.2) |
| | C(1) | C(4) | 109.4 (1.2) | | C(1*) | C(4*) | 110.3 (1.2) |
| | C(2) | C(4) | 108.8 (1.2) | | C(2*) | C(4*) | 108.6 (1.1) |
| C(1) | N | C(1*) | 110.6 (1.2) | C(1*) | N* | C(1) | 112.2 (1.2) |
| C(2) | N | C(3) | 112.4 (1.2) | C(2*) | N* | C(3*) | 109.9 (1.3) |
| C(3) | O(1) | O(2) | 125.5 (1.4) | C(3*) | O(1*) | O(2*) | 124.5 (1.8) |
| | O(1) | C(2) | 115.4 (1.2) | | O(1*) | C(2*) | 117.8 (1.4) |
| | O(2) | C(2) | 119.2 (1.5) | | O(2*) | C(2*) | 117.8 (1.6) |
| C(4) | N | C(5) | 112.9 (1.3) | C(4*) | N* | C(5*) | 113.5 (1.2) |
| C(5) | O(3) | O(4) | 121.0 (1.5) | C(5*) | O(3*) | O(4*) | 125.5 (1.5) |
| W(1) | O(2) (V) | O(4) | 120.4 (0.8) | W(2) | O(1*) (II) | W(1) | 119.6 (1.1) |
| | O(2) (V) | W(2) | 74.1 (0.8) | | | | |
| | O(4) | W(2) | 94.3 (0.9) | | | | |

[a] Estimated standard deviations calculated[20] from the variance–covariance matrix obtained in the final least-squares cycle are given in parantheses. [b] Roman numerals refer to unit cell translations indicated in Table III.

tively.) Thus, as in the CoY⁻ ion[3] and the Mn(OH)₂-Y[2-] and Fe(OH₂)Y⁻ aquo complexes,[4,5] the ring is distorted from planarity while maintaining an approximate $C_2$ axis. The degree of nonplanarity is indicated in Table V (plane 10) and by the sum of internal angles, 514.0°, substantially less than the 540° in a planar ring. Approximate preservation of tetrahedral bond angles at nitrogen requires simultaneous rotations of the ring systems branching from the nitrogen atoms around the respective tin–nitrogen bonds, leaving the nitrogen lone electron pair directed toward the tin atom. These rotations are in the same directions about both bonds (counterclockwise looking down the nitrogen–tin bonds) and give rise to the nonplanar conformation of the ethylenediamine ring described by the torsion angles around the individual bonds in Table VI. Because the environment of the SnY moiety in these crystals is highly asymmetric, the twofold axis is only approximate as can be seen from Table VII, where distances

to the diad of atoms related by it are compared, and from the view down the twofold axis in Figure 2. Bond angles related by the quasi-twofold axis can be compared in Table IV. Some differences occur, but interestingly most pairs from the inner coordination group agree within experimental accuracy.

The four glycinate rings are divided into structurally distinct pairs: one pair is roughly perpendicular to and the other nearly copolanar with the ethylenediamine ring. The first pair, which contain C(5) and C(5*), are reasonably planar as indicated by sums of internal angles of 530.6 and 537.2°, respectively, whereas in the latter rings, which contain C(3) and C(3*), the sums of internal angles are, respectively, 520.3 and 523.1°. The deviations from planarity are further described by least-squares planes 6–9 in Table V and by the torsion angles around the nitrogen–carbon bonds in Table VI.

Distortions from a least-squares plane through the

## TABLE V
### LEAST-SQUARES PLANES[a,b]

| Atom | 1[c] | 2[c] | 3[c] | 4[c] | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | O(1) | O(3) | O(1*) | O(3*) | Sn(2) | Sn(2) | Sn(2) | Sn(2) | Sn(2) | Sn(2) |
| 2 | O(2) | O(4) | O(2*) | O(4*) | O(1) | O(1) | O(1*) | O(3) | O(3*) | N |
| 3 | C(2) | C(4) | C(2*) | C(4*) | O(1*) | N | N* | N | N* | N* |
| 4 | C(3) | C(5) | C(3*) | C(5*) | N | C(2) | C(2*) | C(4) | C(4*) | C(1) |
|   |   |   |   | $(x + 1, y, z + 1)$ |   |   |   |   |   |   |
| 5 | Sn(1) | Sn(1) | Sn(1) | Sn(1) | N* | C(3) | C(3*) | C(5) | C(5*) | C(1*) |
|   | $(x, y, z)$ | $(x, y, z)$ | $(x + 1, y + 1, z + 1)$ |   |   |   |   |   |   |   |
| 6 | Sn(1) | Sn(2) | Sn(2) | Sn(2) |   |   |   |   |   |   |
|   | $(x, y, z + 1)$ |   |   |   |   |   |   |   |   |   |
| $m_1$ | 5.356 | 5.648 | 7.180 | 0.076 | 5.929 | 6.204 | 6.500 | 5.656 | 0.464 | 5.820 |
| $m_2$ | −1.124 | 0.302 | −4.213 | 5.179 | −4.493 | −2.522 | −3.951 | 1.357 | 5.671 | −4.313 |
| $m_3$ | 4.882 | −4.044 | 2.144 | 4.631 | 3.929 | 4.141 | 3.498 | −3.559 | 4.060 | 4.117 |
| $d$ | 5.579 | 0.285 | 4.290 | 5.126 | 4.692 | 5.333 | 4.898 | 0.759 | 5.143 | 4.736 |
| $\Delta d,1$ | −0.001 | −0.011 | −0.007 | 0.076 | −0.133 | 0.190 | −0.197 | −0.146 | 0.118 | −0.028 |
| $\Delta d,2$ | −0.001 | −0.012 | 0.007 | 5.179 | 0.122 | −0.205 | 0.192 | 0.145 | −0.114 | −0.092 |
| $\Delta d,3$ | −0.001 | −0.010 | −0.005 | 4.631 | −0.013 | −0.336 | 0.368 | 0.223 | −0.199 | 0.182 |
| $\Delta d,4$ | 0.002 | 0.032 | 0.019 | 5.126 | −0.109 | 0.278 | −0.337 | −0.214 | 0.188 | 0.259 |
| $\Delta d,5$ | −0.70 | −0.28 | 0.82 |   | 0.134 | 0.073 | −0.025 | −0.008 | 0.007 | −0.321 |
| $\Delta d,6$ | 0.55 |   | −0.40 | −0.37 |   |   |   |   |   |   |

[a] The planes are defined in by the equation $m_1 x + m_2 y + m_3 z = d$. [b] $\Delta d,i$ refers to the deviation in ångströms of atom $i$ from the least-squares plane. [c] This least-squares plane is determined by atoms 1–4.

## TABLE VI
### TORSION ANGLES IN $Sn^{II}_2 Y \cdot 2H_2O$

| | | | |
|---|---|---|---|
| N–C(1)–C(1*)–N* | 59° 13′ | Sn(2)–N*–C(2*)–C(3*) | 52° 31′ |
| Sn(2)–N–C(1)–C(1*) | −52° 54′ | Sn(2)–N–C(4)–C(5) | 58° 50′ |
| C(1)–C(1*)–N*–Sn(2) | −47° 57′ | Sn(2)–N*–C(4*)–C(5*) | 61° 05′ |
| Sn(2)–N–C(2)–C(3) | 47° 48′ | | |

## TABLE VII
### DISTANCES OF ATOMS TO THE QUASI-TWOFOLD AXIS (Å)

| Atom | Distance | Atom | Distance |
|---|---|---|---|
| O(1) | 2.67 | O(1*) | 2.59 |
| O(2) | 4.62 | O(2*) | 4.58 |
| O(3) | 2.15 | O(3*) | 2.29 |
| O(4) | 3.88 | O(4*) | 3.94 |
| N | 1.49 | N* | 1.48 |
| C(1) | 0.75 | C(1*) | 0.75 |
| C(2) | 2.77 | C(2*) | 2.78 |
| C(3) | 3.43 | C(3*) | 3.35 |
| C(4) | 2.51 | C(4*) | 2.46 |
| C(5) | 2.71 | C(5*) | 2.74 |

equatorial atoms of the SnY pentagonal bipyramid are listed in Table V (plane 5). The nitrogen–oxygen contacts in the equatorial plane of the coordination polyhedron are quite short: 2.68 ± 0.02 and 2.72 ± 0.02 Å for O(1)–N and O(1*)–N*, respectively, but the remaining nine edges do not show any unusual crowding (Table VIII). Again the approximation to $C_2$ symmetry appears to hold better for the tighter interatomic contacts.

The spread in carbon–nitrogen and carbon–carbon bond lengths does not exceed $3\sigma$. The average values of 1.51 Å for both carbon–nitrogen and carbon–carbon (including ethylenediamine) bonds may be compared with accepted[28] values of 1.47 Å for carbon–nitrogen

## TABLE VIII
### DISTANCES OF THE INNER COORDINATION GROUP (Å)[a]

| Edge | Length | Edge | Length |
|---|---|---|---|
| O(1)–O(3) | 3.72 (2) | O(1*)–O(3*) | 3.67 (2) |
| O(1)–O(3*) | 3.55 (2) | O(1*)–O(3) | 3.77 (2) |
| O(1)–N | 2.68 (2) | O(1*)–N* | 2.72 (2) |
| O(3)–N | 2.76 (2) | O(3*)–N* | 2.79 (2) |
| O(3*)–N | 2.95 (2) | O(3)–N* | 3.04 (2) |
| N–N* | 2.96 (2) | | |

[a] See footnote $b$ of Table II.

(28) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 18** (1965).

and 1.51 Å for $C(sp^2)$–$C(sp^3)$ bonds. Bond angles around the $sp^3$ hybridized atoms of the ethylenediamine and acetate groups are close to the ideal tetrahedral value.

**B. Bonding of the Carboxylate Groups.**—Carboxylate groups act as bifunctional ligands, and even for the C(3), C(3*), and C(5*) carboxylate groups, which coordinate with more than two tin atoms, the stronger bonds always form a link from Sn(1) to Sn(2). Except for the carboxylate group at C(5), the coordination to Sn(1) is stronger (shorter) than to Sn(2). In the case of the carboxylate group containing C(3), one oxygen atom, O(1), is itself bifunctional and forms strong bonds with Sn(1) as well as Sn(2).

All carboxylate groups are planar within experimental accuracy: the sums of the bond angles at the central carbon atoms C(3), C(5), C(3*), and C(5*) are 360.1, 359.7, 359.9, and 360.9°, respectively. Somewhat surprisingly, the tin atoms most strongly coordinated to the carboxylate groups are not coplanar with them, as can be seen from Table V, planes 1–4.

Differences in the carbon–oxygen bond lengths (1.22–1.29 Å) are of limited significance in view of their fairly large standard deviations (±0.02 Å); however all values are within the range reported for carboxylic acids and esters[28] (1.23 and 1.31 Å for the shorter and longer bonds, respectively). The relatively small spread arises from the bifunctional role of the carboxylate groups in the structure and from the weakness of the tin–oxygen interactions. The differences that do appear will be shown to be consistent with the relatively larger variations in the tin–oxygen distances.

At Sn(1), the Sn–O bond lengths vary from 2.14 ± 0.01 to 2.59 ± 0.01 Å for the more strongly coordinated atoms and from 3.10 ± 0.01 to 3.18 ± 0.01 Å for the weaker interactions. At Sn(2), the tin–oxygen bonds fall between 2.29 ± 0.01 and 2.70 ± 0.01 Å. These large variations are confirmed by our independent refinement of the Cu $K\alpha$ data described in the Appendix (see Table IX).

O(1) is bound to Sn(1) at $(x, y, z + 1)$ at a distance of 2.18 ± 0.01 Å and to Sn(2) $(2.70 \pm 0.01$ Å), while O(2) forms a very weak bond with Sn(1) at $(x, y, z + 1)$ $(3.18 \pm 0.01$ Å) and is within hydrogen-bonding dis-

TABLE IX
Tin–Oxygen Distances Obtained from Cu Kα Data (Å)$^a$

| | | | |
|---|---|---|---|
| Sn(1)–O(1) (II) | 2.18 (1) | Sn(1)–O(4*) (III) | 2.15 (1) |
| Sn(1)–O(2) (II) | 3.20 (2) | Sn(2)–O(1) | 2.69 (1) |
| Sn(1)–O(4) | 2.54 (1) | Sn(2)–O(3) | 2.27 (1) |
| Sn(1)–O(1*) (IV) | 3.11 (2) | Sn(2)–O(1*) | 2.59 (2) |
| Sn(1)–O(2*) (IV) | 2.30 (1) | Sn(2)–O(3*) | 2.44 (1) |
| Sn(1)–O(3*) (III) | 3.14 (1) | | |

$^a$ See footnotes $a$ and $b$ of Table III.

tance from W(1) at $(x, y - 1, z + 1)$ (2.79 ± 0.03 Å). The carbon–oxygen distances of 1.29 ± 0.02 and 1.29 ± 0.02 Å to O(1) and O(2), respectively, reflect the more pronounced carbonyl character in the C(3)–O(2) bond, consistent with the longer tin–oxygen distance. The pattern of strong bonding around O(1) is further supported by the individual bond angles of 125.3 ± 0.5, 117.7 ± 0.9, and 116.4 ± 0.9° around this atom (Table IV), which are close to the ideal value for sp² hybridization and add up to 359.4° indicating planarity of the ligands. The angles around O(2) do not exhibit a similar regularity and their values are consistent with extremely weak tin–oxygen bonding.

O(3) and O(4) are bonded to Sn(2) at 2.29 ± 0.01 Å and to Sn(1) $(x, y, z)$ at 2.59 ± 0.01 Å, respectively. O(4) forms also a hydrogen bond with W(1) at 2.85 ± 0.02 Å. The weaker tin–oxygen bond generated by O(4) is not compensated for by the hydrogen bonding as reflected in the O(3) and O(4) carbon–oxygen distances of 1.28 ± 0.02 and 1.22 ± 0.02 Å, respectively. However, bonding at O(4) seems strong enough to maintain reasonable angles between the ligands (127.8 ± 1.1, 119.3 ± 0.7, and 112.8 ± 1.2°) and to impose planarity as indicated by the sum of the bond angles of 359.9°. The only angle at O(3), 119.9 ± 1.0° for Sn(2)–O(3)–C(5), is characteristic of sp² hybridization.

O(1*) is within bonding distance from Sn(1) at $(x + 1, y + 1, z + 1)$ (3.10 ± 0.01 Å) and from Sn(2) (2.64 ± 0.01 Å) and hydrogen bonded to W(2) $(x, y, z + 1)$ at 2.71 ± 0.03 Å. Other than C(3*), Sn(1) $(x + 1, y + 1, z + 1)$ at 2.30 ± 0.01 Å is the only atom bonded to O(2*). The nearly equal carbon–oxygen bond lengths of 1.23 ± 0.02 and 1.25 ± 0.02 Å to O(1*) and O(2*), respectively, are consistent with the three weak bonds to O(1*) and only one bond, of greater strength, to O(2*). At O(1*) only the Sn(2)–O(1*)–C(3*) angle of 115.9 ± 1.1°, defined by the strongest bonds to this atom, is close to the sp² value. At O(2*) the Sn(1)–O(2*)–C(3*) angle of 112.5 ± 1.2° is reasonably close to the sp² value.

O(3*) forms a very weak bond with Sn(1), $(x + 1, y, z + 1)$ at 3.14 ± 0.01 Å and a moderately strong bond with Sn(2) (2.45 ± 0.01 Å); O(4*) is tightly coordinated to Sn(1) $(x + 1, y, z + 1)$ at 2.14 ± 0.01 Å. This bonding pattern is reflected in the C(5*)–O(3*) and C(5*)–O(4*) bond lengths of 1.22 ± 0.02 and 1.29 ± 0.02 Å, respectively, the latter value corresponding to a very strong tin–oxygen bond. As before, only the more strongly coordinated ligands support angles close to 120°: Sn(2)–O(3*)–C(5*) (117.1 ± 1.0°) and Sn-(1)–O(4*)–C(5*) (118.1 ± 1.0°). Although the angles formed at O(3*) by the weaker bonds are 171.4 ± 0.5 and 71.1 ± 0.9°, it is interesting to note that the sum of all angles at this atom is 359.6°.

The correlation of carbon–oxygen with tin–oxygen bond lengths within the individual carboxylate groups

can be extended to a comparison among different carboxylate groups. From the above discussion O(2), O(4), O(1*), and O(3*) appear to have additional carbonyl character (carbon–oxygen distances not larger than 1.23 Å); they correspond to tin–oxygen interactions above 2.45 Å. The shortest carbonyl bond is found for O(2) (1.20 Å), which has only one very weak tin–oxygen interaction (3.18 Å) and one hydrogen bond. O(4) and O(3*) each have carbon–oxygen bond lengths of 1.22 Å: besides having similar interactions with tin (the distances are 2.59 and 2.45 Å, respectively), O(4) is hydrogen bonded to W(1) and O(3*) has an additional weak tin–oxygen interaction (3.14 Å). O(1*), which is only weakly coordinated to two tin atoms (at 2.64 and 3.10 Å) and a water molecule, displays the largest carbon–oxygen distance (1.23 Å) in this group. O(1), O(3), O(2*), and O(4*) approach a state where oxygen forms two single bonds: a carbon–oxygen bond between 1.25 and 1.29 Å and a tin–oxygen bond between 2.14 and 2.30 Å; as expected the stronger tin–oxygen coordinations (2.14 and 2.18 Å) result in the weaker carbon–oxygen bonds (1.29 Å).

**C. Geometry at the Eight-Coordinated Tin.** —The configuration at Sn(1) is highly irregular and appears to stem from the constraints imposed by its role as a bridging agent between four different SnY units in a three-dimensional periodic structure. Its geometry, shown in Figure 3, can be pictured as two interlocked tetrahedra, one severely elongated and the other severely flattened. Thus, Sn(1) sits above a triangle of three nearest oxygen atoms O(4*) $(x - 1, y, z - 1)$, O(1) $(x, y, z - 1)$, and O(2*) $(x - 1, y - 1, z - 1)$ at distances of 2.14 ± 0.01, 2.18 ± 0.01, and 2.30 ± 0.01 Å, respectively. These ligands form the basal plane of the elongated tetrahedron where the tin lone electron pair is inferred to occupy the remaining vertex. The interatomic contacts of 2.72 ± 0.02 Å for O(1)–O(4*), 2.84 ± 0.02 Å for O(2*)–O(4*), and 2.92 ± 0.02 Å for O(1)–O(2*) along the edges of the oxygen triangle support angles at Sn(1) of 77.9 ± 0.4, 79.4 ± 0.5, and 81.2 ± 0.4°, respectively. Weaker tin–oxygen bonds of 2.59 ± 0.01 Å to O(4) $(x, y, z)$, 3.10 ± 0.01 Å to O(1*) $(x - 1, y - 1, z - 1)$, 3.14 ± 0.01 Å to O(3*) $(x - 1, y, z - 1)$, and 3.18 ± 0.01 Å to O(2) $(x, y, z - 1)$ occur in an outer coordination set of four oxygen atoms, forming the flattened tetrahedron with angles of 143.0 ± 0.3° for O(2)–Sn(1)–O(3*) and 164.3 ± 0.4° for O(4)–Sn(1)–O(1*), respectively. This tetrahedron is interlocked with the inner coordination tetrahedron in a manner that allows room for the lone electron pair. We note that the bond to O(4) is still comparable in strength to Sn–O bonds within the SnY group.

**D. Water Molecules.**—Both water molecules, although not coordinated directly to either structural class of tin, contribute, through hydrogen bonding, to the three-dimensional linking which lends stability to the crystalline arrangement (Figure 4). W(1) is hydrogen bonded to W(2) at 2.82 ± 0.03 Å and is also linked to the adjacent SnY moieties at $(x, y, z)$ and $(x, y + 1, z - 1)$ through hydrogen bonds with the carboxylate oxygens O(4) and O(2), respectively. W(2) is hydrogen bonded *via* O(1*) to SnY groups at $(x, y, z - 1)$.

**E. Summary of Solid-State Structure.**—The SnY moieties are coordinated to Sn(1) atoms at $(x, y, z)$
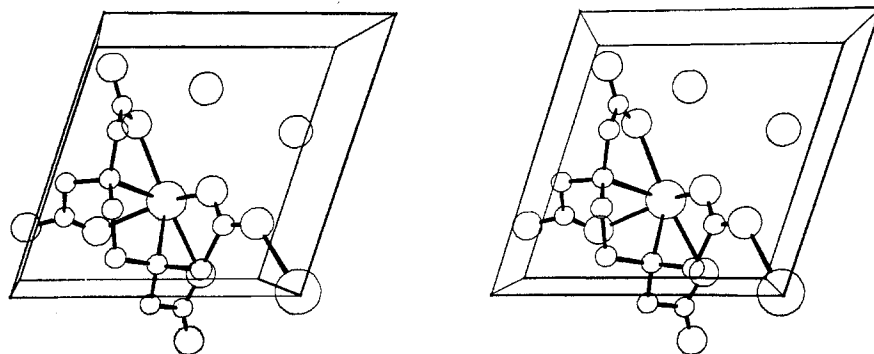
Figure 5.—Three-dimensional view of a unit cell of distannous ethylenediaminetetraacetate dihydrate down the z axis. The y axis is vertical and the x axis is horizontal. Sn(1) is at the origin.

*via* O(4), at $(x, y, z + 1)$ *via* O(1) and O(2), at $(x + 1, y, z + 1)$ *via* O(3*) and O(4*), and at $(x + 1, y + 1, z + 1)$ *via* O(1*) and O(2*) (Figure 5). Sn(2) atoms are trapped inside ethylenediaminetetraacetate groups, but the Sn(1) atoms which act as bridging agents between SnY subunits in adjacent cells at $(x, y, z)$, $(x, y, z - 1)$, $(x - 1, y, z - 1)$, and $(x - 1, y - 1, z - 1)$ cannot be identified with any particular EDTA ligand. In a similar fashion, W(2) is only hydrogen bonded to SnY moieties at $(x, y, z - 1)$, but W(1) links SnY entities at $(x, y, z)$ and $(x, y + 1, z - 1)$. The conformation in the solid might consequently be represented by the appropriate structural formula Sn[SnY·H₂O]-H₂O.

The tin–oxygen bonds linking SnY units *via* Sn(1) are 2.14 and 2.18, 2.14 and 2.30, and 2.18 and 2.59 Å for the x, y, and z directions, respectively. However, the weaker cross-linked y and z directions gain additional strength through hydrogen bonding with water molecules: the hydrogen bonding pattern of W(1) provides extra linking between SnY moieties in the y direction, and a hydrogen-bonding chain SnY···W(1)···W(2)··· SnY exists in the z direction.

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## Appendix

The strong pseudosymmetry encountered during solution of the structure prompted us to verify the analysis through direct phasing by anomalous dispersion methods.[29,30]

Intensity data were obtained from a crystal of dimensions 0.24 × 0.07 × 0.22 mm (in the $a^*$, $b^*$, and $c^*$ directions), mounted with its c axis collinear with the $\phi$ axis of the goniostat. The intensities of $hkl$ and $\bar{h}k\bar{l}$ reflections were measured with Cu Kα radiation (λ 1.5418 Å) selected using the (0002) reflection of a highly oriented graphite crystal monochromator. The X-ray tube was set at a 3° takeoff angle, and angles ranging

(29) S. Rumaseshan in "Advanced Methods of Crystallography," G. N. Ramachandran, Ed., Academic Press, New York, N. Y., 1964, p 67.
(30) G. N. Ramachandran and S. Raman, *Curr. Sci.*, **25**, 348 (1956).

between 2.03 and 2.64° of $2\theta$ were scanned. Background counts of 10 sec were taken at each end of the scan by the stationary-crystal–stationary-counter technique. Attenuators were used to prevent the count rate exceeding 13,000/sec. Experimental reproducibility was monitored on reflection (110). The reciprocal lattice was recorded out to the instrumental limit (sin θ = 0.906), and a total of 2618 reflections in the Cu Kα sphere were measured. Other experimental conditions were as described for the Mo Kα data set.

In order to apply corrections for absorption, the dimensions of the crystal were determined and its faces were identified on the diffractometer. All members of the forms {100}, {010}, and {001} were exhibited. The calculated transmission coefficients, based on a linear absorption coefficient of 268.1 cm⁻¹ for Cu Kα radiation, ranged from 0.032 to 0.248. Data reduction proceeded as for the Mo Kα data, and 31 reflections were denoted absent. From the 2587 reflections above background 1261 Bijvoet pairs could be formed. The anomalous scattering of tin ($\Delta f'' = 5.6$ at (sin θ)/λ = 0 for Cu Kα radiation) was exploited to obtain acentric phases for the $hkl$ member of each pair, following a procedure outlined by Hall and Maslen.[31] These 1252 phases led to an electron density map which unambiguously showed all but one atom belonging to one image only. Some spurious peaks were present close to tin atoms, but the other image was completely absent. The position of W(2) was not revealed but showed up in a subsequent difference Fourier. Two cycles of full-matrix least-squares refinement on 1261 $hkl$ reflections assuming anisotropic thermal parameters reduced $R_1$ from 0.104 to 0.044 and $R_2$ from 0.152 to 0.057. After 29 severely affected reflections were corrected for secondary extinction, refinement was continued in three more cycles of full-matrix least squares on the complete set of 2587 reflections above background, yielding $R_1 = 0.062$ and $R_2 = 0.087$. Although the parameters had not completely converged yet, it was obvious that this structure was identical with the structure obtained from the Mo Kα data (*e.g.*, tin–oxygen bond distances in Tables IV and IX), and refinement was discontinued.

(31) S. R. Hall and E. N. Maslen, *Acta Crystallogr.*, **18**, 265 (1965).