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The Crystal Structure of Stannic Ethylenediaminetetraacetate Monohydrate

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The crystal structure of stannic ethylenediaminetetraacetate monohydrate, $C_{10}H_{14}N_2O_9Sn$, has been determined by a single-crystal three-dimensional X-ray diffraction study. The compound crystallizes in space group $P2_1/c$ with four formula units in each unit cell of dimensions $a = 13.768 \pm 0.005$, $b = 7.058 \pm 0.003$, $c = 13.471 \pm 0.005$ Å, and $\beta = 91.44 \pm 0.02°$. The calculated and observed densities are 2.156 and 2.150 g cm^{-3}, respectively. The intensity data were obtained on a Picker automatic diffractometer (Mo Kα radiation, λ 0.71069 Å), and the structure was solved by the heavy-atom method. Full-matrix least-squares refinement of all position parameters, hydrogen isotropic temperature factors, and anisotropic thermal parameters for all other atoms converged to a discrepancy index $R = 4.1\%$ for 2843 reflections above background. Tin(IV) is coordinated by the two nitrogen atoms and four carboxylate oxygens of the hexadentate ethylenediaminetetraacetate ligand and by the water molecule to form a seven-coordinate aquo complex. An approximate C_2 axis passes through the OH_2 ligand, the Sn atom, and the midpoint of the C–C bond of the ethylenediamine moiety. The average Sn–O bond distance is 2.083 Å for the four carboxylate oxygens, the two Sn–N bonds average 2.313 Å, and the tin–water distance is 2.124 Å.

Introduction

Langer has described the preparation of stable 1:1 complexes of ethylenediaminetetraacetic acid with certain tetravalent metal ions.[1] Among these is the compound $Sn^{IV}(OH_2)Y$ (H_4Y = ethylenediaminetetraacetic acid, EDTA). The structures proposed for these complexes were based on chemical and spectral data with the ancillary assumption that the maximum coordination number of tin was 6. A number of considerations have led us to question this assumption. These evolve from what is now known about the geometries of EDTA chelates and from the nature of valence shell expansion in tin(IV) compounds.

While most organotin(IV) compounds have four-coordinate tetrahedral structures,[2-4] expanded octet bonding usually occurs in the form of five-coordinate trigonal-bipyramidal[5-9] or six-coordinate octahedral[9-14] geometries. However, higher coordination numbers have been observed. For example, seven-coordinate pentagonal-bipyramidal[15] and eight-coordinate dodecahedral[16] configurations have recently been reported for tin(IV). A recent crystallographic study[17] of $Sn^{II}_2Y \cdot 2H_2O$ has indicated the presence of two fundamentally different Sn(II) atoms, both of which exhibit high coordination numbers: one tin is the nucleus of a hexadentate ψ-seven-coordinate SnY moiety,[18] while the second, which functions as a bridge between the SnY units, is ψ eight-coordinate.[18] Moreover, the configuration of the SnY substructure in this tin(II) complex closely resembles the geometries of the $Mn(OH_2)Y^{2-}$ [19] and $Fe(OH_2)Y^{-}$ [20] ions as determined for their crystalline acid salts. The identical stoichiometries of the $Sn^{IV}(OH_2)Y$ complex and the ionic species above strongly suggest that this tin(IV) chelate may exhibit seven-coordination with the aquo ligand replacing the lone pair in the $Sn^{II}Y$ structure.

The three-dimensional single-crystal X-ray study of $Sn^{IV}(OH_2)Y$ reported below was performed to test this hypothesis and to expand our knowledge of the structures of EDTA complexes with tetravalent ions.

Experimental Section

A sample of tin(IV) ethylenediaminetetraacetate monohydrate, $Sn^{IV}(OH_2)Y$, was kindly supplied by H. G. Langer. The colorless crystals are stable to air and to X-radiation. The reciprocal lattice symmetry (C_{2h}; $2/m$), observed from preliminary Weissenberg photographs taken with Cu Kα radiation, indicated that the crystals belong to the monoclinic system. Systematic absences, occurring for $h0l$ reflections, when $l = 2n + 1$, and for the $0k0$ reflections, when $k = 2n + 1$, are consistent only with space group $P2_1/c$.

Intensity data were collected from a well-formed needlelike crystal of dimensions 0.15 × 0.92 × 0.34 × 0.29 mm (perpendicular to the {100}, {010}, {001}, and {102} faces, respectively) sealed in a 0.3-mm thin-wall glass capillary. This crystal was carefully centered on a Picker four-circle automatic diffractometer and aligned with its b (needle) axis collinear with ϕ. Lattice constants were calculated by least-squares refinement of the setting angles of 18 reflections (Mo Kα radiation, λ 0.71069 Å). The cell parameters $a = 13.768 \pm 0.005$, $b = 7.058 \pm 0.003$, $c = 13.471 \pm 0.005$ Å, and $\beta = 91.44 \pm 0.02°$ give a unit cell volume of 1308.7 Å^3 and a calculated density of 2.156 g cm^{-3} for $C_{10}H_{14}N_2O_9Sn$ with $Z = 4$. The observed density measured by flotation in a mixture of ethylene dibromide and ethylene chlorobromide at 23° is 2.150 ± 0.005 g cm^{-3}. The estimated standard deviations of the lattice constants, as computed in the least-squares analysis, were a factor of 10 better than the errors assigned above, which reflect our experience with systematic errors and reproducibility of results under different experimental conditions.

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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	0.75040 (2)	0.54625 (3)	0.46303 (2)	21.5 (0.2)	44.6 (0.6)	22.4 (0.2)	4.0 (0.2)	2.1 (0.1)	1.8 (0.2)
O(1)	0.6168 (2)	0.5754 (4)	0.5322 (2)	26 (2)	68 (5)	31 (2)	8 (2)	6 (1)	6 (2)
O(2)	0.5063 (3)	0.7934 (5)	0.5648 (3)	49 (2)	95 (7)	52 (2)	19 (3)	25 (2)	−0 (3)
O(3)	0.7163 (2)	0.3317 (4)	0.3613 (2)	34 (2)	79 (6)	42 (2)	10 (3)	−8 (1)	−18 (3)
O(4)	0.6295 (2)	0.2439 (5)	0.2285 (2)	36 (2)	110 (7)	46 (2)	−6 (3)	1 (2)	−35 (3)
O(1*)	0.8859 (2)	0.4191 (4)	0.4571 (2)	27 (2)	79 (6)	32 (2)	16 (2)	3 (1)	10 (2)
O(2*)	1.0068 (3)	0.3494 (6)	0.3572 (2)	45 (2)	178 (9)	41 (2)	53 (4)	9 (2)	−0 (3)
O(3*)	0.7816 (2)	0.7695 (5)	0.5589 (2)	31 (2)	99 (6)	28 (1)	−7 (3)	7 (1)	−13 (3)
O(4*)	0.8618 (3)	1.0353 (4)	0.5908 (2)	44 (2)	64 (6)	39 (2)	5 (3)	−6 (2)	−10 (3)
N	0.6455 (2)	0.6875 (5)	0.3504 (2)	24 (2)	47 (6)	23 (2)	3 (3)	3 (1)	1 (2)
N*	0.8483 (2)	0.7499 (5)	0.3734 (2)	25 (2)	59 (6)	22 (2)	2 (3)	3 (1)	2 (3)
C(1)	0.6995 (3)	0.7823 (6)	0.2692 (3)	33 (2)	81 (8)	23 (2)	−1 (4)	0 (2)	14 (3)
C(2)	0.5858 (3)	0.8171 (6)	0.4097 (3)	28 (2)	47 (7)	34 (2)	14 (3)	3 (2)	−4 (3)
C(3)	0.5663 (3)	0.7259 (6)	0.5105 (3)	25 (2)	54 (7)	34 (2)	1 (3)	4 (2)	−5 (3)
C(4)	0.5856 (3)	0.5329 (6)	0.3074 (3)	27 (2)	67 (8)	29 (2)	1 (3)	−2 (2)	−6 (3)
C(5)	0.6471 (3)	0.3556 (6)	0.2961 (3)	27 (2)	60 (7)	34 (2)	−4 (3)	4 (2)	−10 (3)
C(1*)	0.7896 (3)	0.8806 (6)	0.3097 (3)	30 (2)	60 (7)	29 (2)	−1 (3)	3 (2)	11 (3)
C(2*)	0.9116 (3)	0.6213 (7)	0.3169 (3)	34 (2)	85 (8)	29 (2)	13 (4)	9 (2)	1 (4)
C(3*)	0.9390 (3)	0.4502 (6)	0.3802 (3)	31 (2)	98 (9)	26 (2)	18 (4)	−1 (2)	−4 (3)
C(4*)	0.9058 (3)	0.8590 (7)	0.4477 (3)	28 (2)	80 (8)	30 (2)	−14 (4)	−1 (2)	0 (3)
C(5*)	0.8461 (3)	0.8956 (6)	0.5386 (3)	26 (2)	63 (7)	27 (2)	2 (3)	−5 (2)	−1 (3)
W	0.7566 (3)	0.3545 (6)	0.5846 (2)	42 (2)	142 (8)	37 (2)	35 (3)	16 (2)	40 (3)

Hydrogens	x	y	z	B, Å^2	Hydrogens	x	y	z	B, Å^2
H(11)	0.716 (4)	0.671 (10)	0.224 (4)	4.2 (1.3)	H(1*2)	0.772 (4)	0.980 (8)	0.355 (4)	2.2 (1.0)
H(12)	0.650 (4)	0.887 (7)	0.226 (3)	1.8 (0.9)	H(2*1)	0.971 (5)	0.675 (10)	0.300 (4)	4.2 (1.6)
H(21)	0.526 (4)	0.843 (9)	0.378 (4)	3.1 (1.2)	H(2*2)	0.870 (5)	0.566 (8)	0.253 (5)	3.8 (1.4)
H(22)	0.617 (4)	0.932 (8)	0.419 (4)	2.4 (1.1)	H(4*1)	0.959 (4)	0.791 (9)	0.469 (4)	2.7 (1.1)
H(41)	0.561 (4)	0.566 (8)	0.251 (4)	2.8 (1.2)	H(4*2)	0.925 (5)	0.968 (10)	0.426 (5)	4.7 (1.6)
H(42)	0.532 (4)	0.501 (7)	0.350 (3)	1.2 (0.8)	H(W1)	0.791 (4)	0.228 (9)	0.581 (4)	3.5 (1.3)
H(1*1)	0.825 (3)	0.928 (6)	0.257 (3)	0.5 (0.7)	H(W2)	0.706 (5)	0.329 (10)	0.627 (5)	4.8 (1.7)

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

The intensities of 2995 independent reflections were measured using the θ–2θ scan mode of the diffractometer and Mo Kα radiation selected using the (0002) reflection of a highly oriented graphite crystal monochromator. The X-ray tube was set at a 3° takeoff angle, and a scintillation detector was placed 32 cm from the crystal with an aperture 6.0 mm square. Attenuators were used to prevent the count rate from exceeding 12,000/sec and 1.5-mm incident- and exit-beam collimators were employed to restrict stray radiation. Angles of $2.00 + \Delta°$ were scanned at a speed of 2°/min (Δ is the separation of the Kα doublet), and stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. The reciprocal lattice was recorded out to the limit of the Cu Kα sphere ($\sin\theta = 0.461$). The (3,1,3) reflection, monitored every 50 measurements, showed good stability (±1%).

An error

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

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's are the intensities corrected for Lorentz–polarization and absorption effects. The Lorentz–polarization factors were calculated by the expression $(Lp)^{-1} = \sin 2\theta(1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta_m \cos^2 2\theta)$, where $2\theta_m$ is the monochromator setting angle.[21] 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}, {001}, and {102} were exhibited. The calculated transmission coefficients,[22] based on a linear absorption coefficient of 20.2 cm^{-1} for Mo Kα radiation, ranged from 0.346 to 0.771. The 152 reflections for which either $I < 0$ or $I < 2\sigma(I)$ were denoted absent and were omitted from the structure analysis.

Solution and Refinement of the Structure[23]

An absolute scale factor and an overall temperature factor were computed by Wilson's method. The position of the tin atom was determined from a normal-sharpened three-dimensional Patterson function.[23a] The locations of the remaining nonhydrogen atoms were obtained from a subsequent electron density synthesis.[23a] Least-squares refinement of the atomic positions and isotropic temperature factors on a small computer,[23b] using blocks of 72 variables and a truncated data set of 1950 reflections, reduced

$$R_1 = \frac{\sum||F_o| - |F_c||}{\sum|F_o|}$$

from its initial value of 0.27 to 0.078 and

$$R_2 = \left\{\frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^2}\right\}^{1/2}$$

from 0.30 to 0.096. A difference map[23a] was now calculated, which clearly revealed all hydrogen atoms at reasonable bond distances. Six subsequent cycles of refinement[23b] in which positional and thermal pa-

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[23] Programs and computers used in this study are as follows: (a) M. A. Neuman, "A Crystallographic Fourier Summation Program" (IBM 1130); (b) F. P. van Remoortere and F. P. Boer, "A Full-Matrix Crystallographic Least-Squares Program for the IBM 1130;" (c) J. Gvildys, "A Fortran Crystallographic Least-Squares Refinement Program," based on ORFLS, Program Library 14E7043, Argonne National Laboratory, Applied Mathematics Division, Argonne, Ill., March 31, 1967 (CDC 6600); (d) J. Gvildys, "Two- and Three-Dimensional Crystallographic Fourier Summation Program," based on MIFRI, Program Library B-149, Argonne National Laboratory, Argonne, Ill., April 13, 1965 (CDC 6600); (e) C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 1965 (CDC 6600); (f) J. Gvildys, "ANLFFE, A Fortran Crystallographic Function and Error Program," based on ORFFE, Program Library B-115, Argonne National Laboratory, Argonne, Ill., Sept 17, 1964 (CDC 6600).

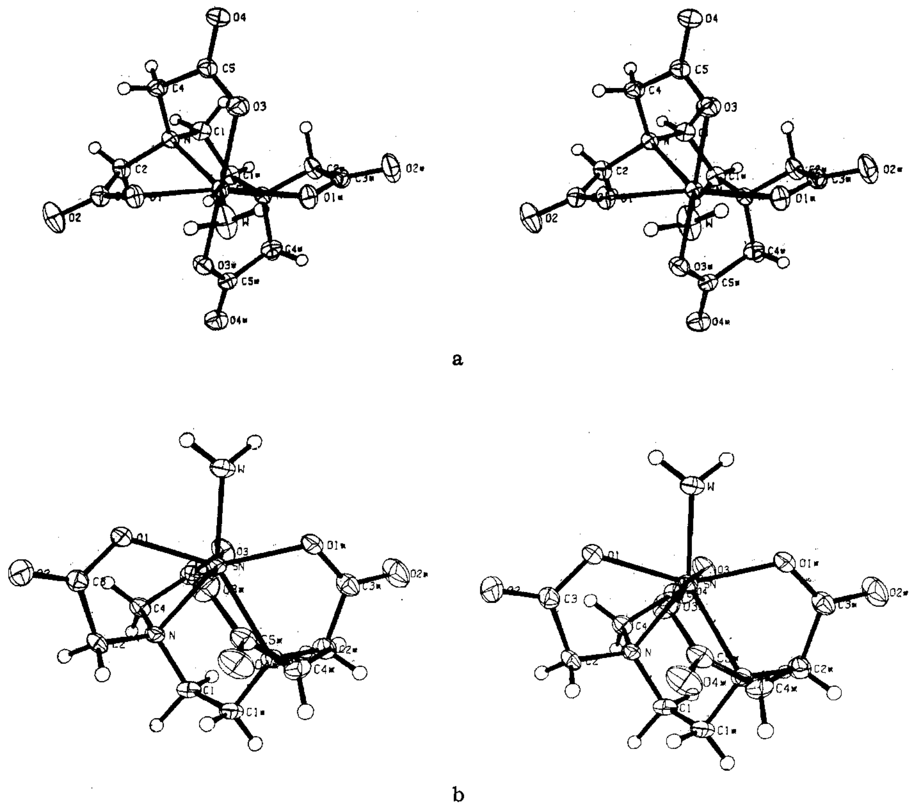

Figure 1.—Three-dimensional view of $Sn^{IV}(OH_2)Y$ showing ellipsoids of thermal motion drawn at 50% probability.

rameters of hydrogen atoms were varied simultaneously with the thermal parameters of adjacent heavier atoms decreased R_1 and R_2 to 0.073 and 0.0875, respectively. Refinement was completed[23c] on a larger computer applying full-matrix least-squares on all 2843 reflections above background and assuming anisotropic temperature factors for the nonhydrogen atoms. After the first cycle, in which R_1 was reduced from 0.076 to 0.049 and R_2 from 0.091 to 0.053, 30 strong low-order reflections, systematically less than their calculated values, were corrected for secondary extinction.[24] After introduction of these corrected values, additional refinement[23c] on all parameters converged in three more cycles to the final discrepancy indices of $R_1 = 0.041$ and $R_2 = 0.051$. Average and maximum shifts in the final least-squares cycle were 0.01σ and 0.04σ, respectively, for nonhydrogen positional parameters, 0.01σ and 0.08σ for the anisotropic thermal parameters, 0.05σ and 0.23σ for hydrogen positions, and 0.16σ and 0.45σ for hydrogen isotropic temperature factors. A final difference map[23d] revealed residual electron density as high as 2.9 $e^- \text{Å}^{-3}$ and negative peaks with absolute values less than 2.1 $e^- \text{Å}^{-3}$ in the region around the tin atom. No other peaks higher than 0.5 $e^- \text{Å}^{-3}$ were present. Throughout the analysis the scattering factors for neutral O, C, N, and Sn were used with a dispersion correction for tin.[25]

Atomic parameters and their estimated standard deviations are given in Table I. The directions of thermal motion may be inferred from Figure 1, in which the three-dimensional structure of the complex is shown using ellipsoids to represent the anisotropic thermal motion.[23e] 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, together with their standard deviations[23f] computed from the variance-covariance matrix obtained in the final least-

TABLE II

ROOT-MEAN-SQUARE DISPLACEMENTS ALONG THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS (Å)[a,b]

Atom	Axis 1	Axis 2	Axis 3
Sn	0.1041 (8)	0.1382 (6)	0.1498 (6)
O(1)	0.125 (5)	0.148 (5)	0.181 (4)
O(2)	0.131 (6)	0.174 (5)	0.265 (5)
O(3)	0.129 (6)	0.165 (5)	0.219 (4)
O(4)	0.128 (6)	0.187 (5)	0.231 (5)
O(1*)	0.119 (6)	0.162 (5)	0.188 (4)
O(2*)	0.127 (6)	0.196 (5)	0.266 (5)
O(3*)	0.137 (5)	0.156 (5)	0.192 (5)
O(4*)	0.122 (6)	0.180 (5)	0.217 (5)
N	0.108 (7)	0.139 (5)	0.155 (5)
N*	0.121 (6)	0.137 (5)	0.158 (5)
C(1)	0.119 (7)	0.165 (6)	0.178 (6)
C(2)	0.095 (9)	0.170 (6)	0.178 (6)
C(3)	0.115 (8)	0.153 (6)	0.181 (6)
C(4)	0.128 (8)	0.153 (7)	0.172 (6)
C(5)	0.117 (8)	0.155 (6)	0.186 (6)
C(1*)	0.114 (8)	0.164 (6)	0.175 (6)
C(2*)	0.129 (8)	0.154 (7)	0.199 (6)
C(3*)	0.134 (8)	0.153 (6)	0.191 (6)
C(4*)	0.125 (8)	0.166 (6)	0.177 (7)
C(5*)	0.126 (7)	0.139 (6)	0.174 (6)
W	0.125 (6)	0.155 (5)	0.263 (5)

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

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(25) 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. Hydrogen scattering factors are by R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Table III
Bond Distances (Å)[a]

Tin–Oxygen Distances	
Sn–O(1)	2.093 (3)
Sn–O(3)	2.088 (3)
Sn–O(1*)	2.074 (3)
Sn–O(3*)	2.075 (3)
Sn–W	2.124 (3)
Tin–Nitrogen Distances	
Sn–N	2.296 (3)
Sn–N*	2.329 (3)
Carbon–Carbon Bonds	
C(1)–C(1*)	1.511 (6)
C(2)–C(3)	1.532 (6)
C(4)–C(5)	1.521 (6)
C(2*)–C(3*)	1.520 (6)
C(4*)–C(5*)	1.514 (6)
Carbon–Nitrogen Bonds	
C(1)–N	1.495 (5)
C(2)–N	1.478 (5)
C(4)–N	1.477 (5)
C(1*)–N*	1.485 (5)
C(2*)–N*	1.482 (5)
C(4*)–N*	1.478 (5)
Carbon–Oxygen Bonds	
C(3)–O(1)	1.299 (5)
C(3)–O(2)	1.215 (5)
C(5)–O(3)	1.291 (5)
C(5)–O(4)	1.224 (5)
C(3*)–O(1*)	1.301 (5)
C(3*)–O(2*)	1.220 (5)
C(5*)–O(3*)	1.291 (5)
C(5*)–O(4*)	1.227 (5)
Carbon–Hydrogen Bonds	
C(1)–H(11)	1.02 (7)
C(1) H(12)	1.15 (5)
C(2)–H(21)	0.95 (6)
C(2)–H(22)	0.92 (6)
C(4)–H(41)	0.86 (6)
C(4)–H(42)	0.97 (5)
C(1*)–H(1*1)	0.94 (4)
C(1*)–H(1*2)	0.96 (5)
C(2*)–H(2*1)	0.93 (7)
C(2*)–H(2*2)	1.09 (7)
C(4*)–H(4*1)	0.91 (6)
C(4*)–H(4*2)	0.87 (7)
Oxygen–Hydrogen Bonds	
W–H(W1)	1.01 (6)
W–H(W2)	0.93 (7)

[a] Estimated standard deviations calculated from the variance–covariance matrix in the last least-squares cycle are given in parentheses.

squares cycle, are listed in Tables III and IV, respectively. A listing of observed and calculated structure factors for the final parameters is available to the interested reader.[26]

Geometry of the $Sn^{IV}(OH_2)$ Complex

The results confirm the presence of seven-coordinate tin in the $Sn^{IV}(OH_2)Y$ complex; the structure is analogous in certain respects to the ψ-seven-coordinate[18] SnY entity in crystalline $Sn^{II}{}_2Y \cdot 2H_2O$. Ethylenediaminetetraacetate acts as a hexadentate ligand, using both nitrogen atoms and four carboxylate oxygens to bind tin (Figures 1a and 1b). The approximate C_2 symmetry of the $Sn^{II}Y$ structure is conserved while the lone electron pair of the tin(II) complex is replaced by a water molecule in $Sn^{IV}(OH_2)Y$. A reduction in bond distances to tin also occurs as a consequence of the smaller ion radius associated with the higher oxidation state.

The coordination polyhedron about tin is drawn in Figure 2. A description of this figure in terms of the more symmetrical geometries for seven-coordination appears unprofitable as indicated by the least-squares planes (1–4) in Table V. The large deviations from plane 1 militate against a pentagonal-bipyramidal model, and planes 2–4 suggest that a description in terms of a capped trigonal prism is also inappropriate.[27]

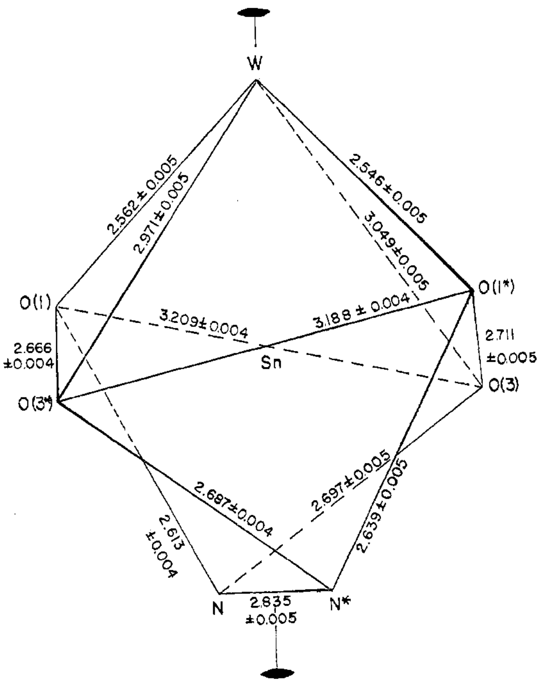

Figure 2.—The coordination polyhedron in $Sn^{IV}(OH_2)Y$.

Several of the interatomic contacts on the edges of the $Sn(OH_2)Y$ coordination polyhedron are fairly close. These include the N···O intra-ring spans (2.613 ± 0.004 to 2.711 ± 0.005 Å), two O···O contacts (O(1)···O(3*), 2.666 ± 0.004 Å, and O(1*)···O(3), 2.7111 ± 0.005 Å), and two contacts involving the water oxygen (W···O(1), 2.562 ± 0.005 Å, and W···O(1*), 2.546 ± 0.005 Å), where asterisks denote atoms related by the approximate noncrystallographic C_2 axis which passes through the tin atom, the water oxygen, and the midpoint of the C(1)–C(1*) bond of the EDTA ligand. These shorter interatomic contacts may in part account for the fact that C_2 symmetry is more closely obeyed in the present structure than for the $Sn^{II}Y$[17] or $Mn(OH_2)Y^{2-}$ [19] species, where longer metal–ligand bonds and interatomic contacts are present. Distances of individual atoms from the quasi-twofold axis are listed in Table VI, the maximum difference for related pairs is only 0.027 Å. Tables III and IV are organized so as to facilitate comparison between distances and angles related by the diad.

Chelation of the metal ion by ethylenediaminetetraacetate results in the formation of five five-membered rings, four of the glycinate type and one based on the ethylenediamine fragment. All show significant deviations from planarity, as indicated by least-squares planes 5–9 of Table V and by the torsion angles summarized in Table VII. Such deviations in fact appear to be typical of hexadentate seven-coordinate complexes of EDTA. A crude measure of the degree of nonplanarity in a five-membered ring can be obtained by summing the five internal angles (Σ_5) and observing the difference from the coplanar value of 540°. For example, in the ethylenediamine ring Σ_5 is 520.3°, slightly above the range (514.0–518.1°) resported for $Mn(OH_2)_2Y^{2-}$,[19] $Fe(OH_2)Y^-$,[20] and $Sn^{II}{}_2Y \cdot 2H_2O$.[17] For the pair of glycinate rings closest to the plane of the ethylene diamine ring (those based on O(1) and O(1*)), Σ_5 has values 520.2 and 522.6°, quite close to the cor-

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[26] 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 St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit \$3.00 for photocopy or \$2.00 for microfiche.

[27] A referee has commented: "Inasmuch as Figure 2 in the manuscript is very like that given for the analogous Mn(II) complex[19] I judge that the hybrid in the crystal carries the larger contribution from capped trigonal-prismatic geometry. The small spread in the four Sn–O bond lengths supports this view; pentagonal-bipyramidal geometry demands a division of these parameters into two sets that may differ by ≥0.10 Å in the Sn–O distance."

TABLE IV
BOND ANGLES (DEG)[a]

Vertex	Atom 1	Atom 2		Vertex	Atom 1	Atom 2	
Sn	N	O(1)	72.9 (0.1)	Sn	N*	O(1*)	73.4 (0.1)
	N	O(3)	75.8 (0.1)		N*	O(3*)	75.0 (0.1)
	N	O(1*)	135.6 (0.1)		N*	O(1)	134.2 (0.1)
	N	O(3*)	101.4 (0.1)		N*	O(3)	103.4 (0.1)
	N	W	143.0 (0.1)		N*	W	141.3 (0.1)
	O(1)	O(3)	100.3 (0.1)		O(1*)	O(3*)	100.4 (0.1)
	O(1)	O(3*)	79.5 (0.1)		O(1*)	O(3)	81.3 (0.1)
	O(1)	W	74.8 (0.1)		O(1*)	W	74.7 (0.1)
	O(3)	W	92.7 (0.2)		O(3*)	W	90.0 (0.1)
	N	N*	75.6 (0.1)		O(1)	O(1*)	149.5 (0.1)
	O(3)	O(3*)	177.1 (0.1)				
O(1)	Sn	C(3)	116.9 (0.3)	O(1*)	Sn	C(3*)	118.8 (0.3)
O(3)	Sn	C(5)	120.1 (0.3)	O(3*)	Sn	C(5*)	121.6 (0.2)
N	Sn	C(1)	111.2 (0.2)	N*	Sn	C(1*)	111.7 (0.2)
	Sn	C(2)	105.1 (0.2)		Sn	C(2*)	104.1 (0.2)
	Sn	C(4)	105.9 (0.2)		Sn	C(4*)	106.1 (0.2)
	C(1)	C(2)	114.3 (0.3)		C(1*)	C(2*)	113.7 (0.3)
	C(1)	C(4)	109.1 (0.3)		C(1*)	C(4*)	110.1 (0.3)
	C(2)	C(4)	110.9 (0.3)		C(2*)	C(4*)	110.8 (0.3)
C(1)	N	C(1*)	111.1 (0.3)	C(1*)	N*	C(1)	110.7 (0.3)
	N	H(11)	102.4 (3.6)		N*	H(1*1)	111.7 (2.5)
	N	H(12)	111.0 (2.4)		N*	H(1*2)	103.0 (3.1)
	C(1*)	H(11)	112.1 (3.5)		C(1)	H(1*1)	109.5 (2.5)
	C(1*)	H(12)	110.8 (2.5)		C(1)	H(1*2)	110.5 (3.2)
	H(11)	H(12)	109.1 (4.0)		H(1*1)	H(1*2)	111.3 (4.0)
C(2)	N	C(3)	109.3 (0.3)	C(2*)	N*	C(3*)	109.9 (0.3)
	N	H(21)	111.6 (3.4)		N*	H(2*1)	114.0 (4.1)
	N	H(22)	110.7 (3.4)		N*	H(2*2)	108.7 (3.4)
	C(3)	H(21)	108.4 (3.3)		C(3*)	H(2*1)	104.3 (4.0)
	C(3)	H(22)	110.0 (3.4)		C(3*)	H(2*2)	106.1 (3.2)
	H(21)	H(22)	106.8 (5.1)		H(2*1)	H(2*2)	113.5 (4.8)
C(3)	O(1)	O(2)	123.6 (0.4)	C(3*)	O(1*)	O(2*)	123.5 (0.4)
	O(1)	C(2)	116.0 (0.3)		O(1*)	C(2*)	116.4 (0.4)
	O(2)	C(2)	120.4 (0.4)		O(2*)	C(2*)	120.1 (0.4)
C(4)	N	C(5)	109.9 (0.3)	C(4*)	N*	C(5*)	110.1 (0.3)
	N	H(41)	110.5 (3.7)		N*	H(4*1)	110.6 (3.6)
	N	H(42)	111.5 (2.8)		N*	H(4*2)	113.8 (4.5)
	C(5)	H(41)	110.3 (3.8)		C(5*)	H(4*1)	106.2 (3.2)
	C(5)	H(42)	107.7 (2.9)		C(5*)	H(4*2)	107.3 (4.6)
	H(41)	H(42)	107.0 (4.7)		H(4*1)	H(4*2)	108.5 (5.8)
C(5)	O(3)	O(4)	123.5 (0.4)	C(5*)	O(3*)	O(4*)	123.0 (0.4)
	O(3)	C(4)	116.3 (0.3)		O(3*)	C(4*)	116.4 (0.4)
	O(4)	C(4)	120.3 (0.4)		O(4*)	C(4*)	120.6 (0.4)
W	Sn	H(W1)	122.0 (3.1)				
	Sn	H(W2)	125.9 (4.2)				
	H(W1)	H(W2)	102.4 (5.2)				

[a] Estimated standard deviations calculated from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses.

responding values for $Sn^{II}_2Y \cdot 2H_2O$. For the glycinate rings based on O(3) and O(3*), Σ_5 has values of 529.2 and 528.0°, respectively, somewhat less than 530.6 and 537.2° for the corresponding rings in the Sn(II) complex.

Within the glycinate rings the Sn–N–C angles, which range from 104.1 ± 0.2 *to* 106.1 ± 0.2°, are reduced significantly below the tetrahedral value. (As a result, the C(1)–N–C(2) and C(1*)–N*–C(2*) angles increase to 114.3 ± 0.3 and 113.7 ± 0.3°, respectively.) Similarly, the internal bond angles at the carboxylate carbons, which vary from 116.0 to 116.4°, are significantly lower than the ideal trigonal angle (whereas the four O–C–O angles average 123.4°). The internal angles at tin are slightly greater for the glycinate rings based on O(3) and O(3*), 75.8 and 75.0°, than those based on O(1) and O(1*), 72.9 and 73.4°. For the ethylenediamine ring, the internal angle at the tin atom is 75.6 ± 0.1° while the angles at N, C(1), C(1*), and N* are all slightly greater than the tetrahedral value.

Unlike the carboxylate groups in $Sn^{II}_2Y \cdot 2H_2O$, which act as bifunctional ligands bridging between tin atoms, each carboxylate group in $Sn^{IV}(OH_2)Y$ is bonded to only one tin atom. The carboxylate groups at C(5) and C(5*) are, however, hydrogen bonded to water *via* their carbonyl oxygens (*vide infra*). The differences in the roles of the carboxylate groups are reflected in the carbon–oxygen bond lengths: their average value of 1.222 ± 0.005 Å in the carbonyls is substantially less than the average of 1.296 ± 0.005 Å for oxygen bonded to tin. The four tin–oxygen bonds average to 2.083 Å; we attach no significance to their individual differences. As observed for $Sn^{II}_2Y \cdot 2H_2O$, all carboxylate groups are planar within experimental accuracy. However, the tin atoms, although strongly coordinated to the carboxyls, are nevertheless not coplanar with them, as may be seen from Table VI, planes 10–13, where tin shows deviations from these planes as large as 0.78 Å. Interestingly, the Sn–O–C angles, which range from 116.9 ± 0.3° to 121.6 ± 0.3°, are all fairly close to the trigonal value.

The Sn–N bond distances average 2.313 Å. The two individual values, 2.296 ± 0.003 and 2.329 ± 0.003 Å, show a surprisingly large difference in view of the ac-

TABLE V
LEAST-SQUARES PLANES[a,b]

	Plane						
	1	2	3	4	5	6	7
Atom 1	Sn	O(1)	O(1)	O(1*)	Sn	Sn	Sn
Atom 2	O(1)	O(1*)	O(3*)	O(3)	N	O(1)	O(1*)
Atom 3	O(1*)	O(3)	N	N	N*	N	N*
Atom 4	N	O(3*)	N*	N*	C(1)	C(2)	C(2*)
Atom 5	N*				C(1*)	C(3)	C(3*)
Atom 6	W						
m_1	2.760	−0.139	−4.613	−4.407	−3.813	7.307	6.831
m_2	5.245	4.625	6.648	1.042	5.134	5.398	3.410
m_3	8.529	−10.168	0.450	12.710	8.549	4.741	9.548
d	8.910	−2.535	1.493	2.060	3.916	10.392	11.624
Δd,1	−0.024	−0.301	−0.274	0.283	−0.015	0.234	−0.215
Δd,2	0.350	−0.298	0.269	−0.278	0.147	−0.256	0.221
Δd,3	−0.367	0.296	0.257	0.266	−0.108	−0.303	0.292
Δd,4	−0.533	0.303	−0.252	−0.270	−0.265	0.242	−0.253
Δd,5	0.550				0.241	0.084	−0.045
Δd,6	0.024						

	Plane					
	8	9	10[c]	11[c]	12[c]	13[c]
Atom 1	Sn	Sn	O(1)	O(3)	O(1*)	O(3*)
Atom 2	O(3)	O(3*)	O(2)	O(4)	O(2*)	O(4*)
Atom 3	N	N*	C(2)	C(4)	C(2*)	C(4*)
Atom 4	C(4)	C(4*)	C(3)	C(5)	C(3*)	C(5*)
Atom 5	C(5)	C(5*)	Sn	Sn	Sn	Sn
m_1	−9.370	−9.750	9.610	8.783	8.340	−9.057
m_2	−2.019	4.247	4.044	3.541	4.006	3.604
m_3	9.315	−4.734	5.548	−8.083	7.304	−7.234
d	−3.947	−7.067	11.208	4.547	12.407	−8.344
Δd,1	0.126	−0.121	−0.001	−0.001	−0.001	−0.004
Δd,2	−0.069	0.070	−0.001	−0.001	−0.002	−0.004
Δd,3	−0.226	0.214	−0.000	−0.001	−0.001	−0.003
Δd,4	0.247	−0.236	−0.002	0.003	0.004	0.012
Δd,5	−0.077	0.072	0.781	0.236	−0.579	0.167

[a] The planes are defined by the equation $m_1x + m_2y + m_3z = d$. [b] $\Delta d,i$ refers to the deviation (in Å) of atom i from the least-squares plane. [c] This least-squares plane is determined by atoms 1–4.

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

Atom	Dist	Atom	Dist	Atom	Dist	Atom	Dist
O(1)	2.016	O(1*)	2.003	C(1)	2.394	C(1*)	2.383
O(2)	4.054	O(2*)	4.081	C(2)	2.441	C(2*)	2.446
O(3)	2.087	O(3*)	2.075	C(3)	2.897	C(3*)	2.906
O(4)	4.003	O(4*)	4.027	C(4)	2.634	C(4*)	2.648
N	1.413	N*	1.422	C(5)	2.835	C(5*)	2.846

TABLE VII
SELECTED TORSION ANGLES IN $Sn^{IV}Y \cdot H_2O$

Atoms	Torsion angle	Atoms	Torsion angle
N–C(1)–C(1*)–N*	−50° 31′	Sn–N*–C(2*)–C(3*)	37° 20′
Sn–N–C(1)–C(1*)	39° 59′	Sn–N–C(4)–C(5)	36° 32′
C(1)–C(1*)–N*–Sn	35° 31′	Sn–N*–C(4*)–C(5*)	34° 35′
Sn–N–C(2)–C(3)	36° 28′		

curacy and symmetry of the structure. The tin–water bond of 2.124 ± 0.003 Å is slightly, but significantly, longer than the average bond length (2.083 Å) for the carboxylate oxygens.

The remaining bond distances are essentially normal. The C–N bonds average 1.483 ± 0.007 Å, in good agreement with the 1.479 ± 0.005 Å cited in the literature for four-covalent nitrogen.[28] The C(1)–C(1*) bond length of 1.511 ± 0.006 Å appears to be slightly shorter than the accepted $C(sp^3)–C(sp^3)$ distance[28] of 1.537 Å, while our average $C(sp^3)–C(sp^2)$ distance of 1.522 ± 0.008 Å is in fair agreement with the accepted value[28] of 1.506 Å for this type of bond. The C–H bond distances, which range from 0.86 ± 0.06 to 1.15 ± 0.05 Å (average 0.96 Å for 12 observations), are subject to the usual systematic shortening from the true internuclear separation, presumably about 1.09 Å, due to the bias of electron density from the hydrogen nucleus toward the bonding region and to the effects of vibrational motion. All of the 30 angles involving hydrogen bonded to carbon fall within two standard deviations of the tetrahedral angle (Table IV).

The O–H bond lengths, 0.93 ± 0.07 and 1.01 ± 0.06 Å, and the H–O–H bond angle, 102 ± 5°, appear quite reasonable in view of the errors involved. These two hydrogen atoms form hydrogen bonds to O(4*) and O(4) of adjacent complexes related by the cell translation on *b* and by the *c* glide, respectively. As a result, infinite two-dimensional hydrogen-bonded networks are formed in the *yz* planes of the crystal. (The crystal packing is shown in Figure 3.) The W···O(4) and

TABLE VIII
DISTANCES AND ANGLES FOR THE W–H···O BONDS[a]

A. Distances, Å			
W–H(W1)	1.01 (6)	W–H(W2)	0.93 (7)
W···O(4)	2.734 (5)	W···O(4*)	2.679 (5)
O(4)···H(W2)	1.82 (7)	O(4*)···H(W1)	1.67 (6)
B. Angles, Deg			
Sn–W–H(W1)	122.0 (3.1)	Sn–W–H(W2)	125.9 (4.2)
S–W···O(4*)	124.8	Sn–W···O(4)	134.0
H(W1)–W–H(W2)	102.4 (5.2)	O(4)···W···O(4*)	96.9
O(4)···H(W2)···W	166.6	O(4*)···H(W1)···W	168.9
C(5)–O(4)···H(W2)	129.1	C(5*)–O(4*)···H(W1)	120.6
C(5)–O(4)···W	124.9	C(5*)–O(4*)···W	124.8

[a] Estimated standard deviations calculated from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses.

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

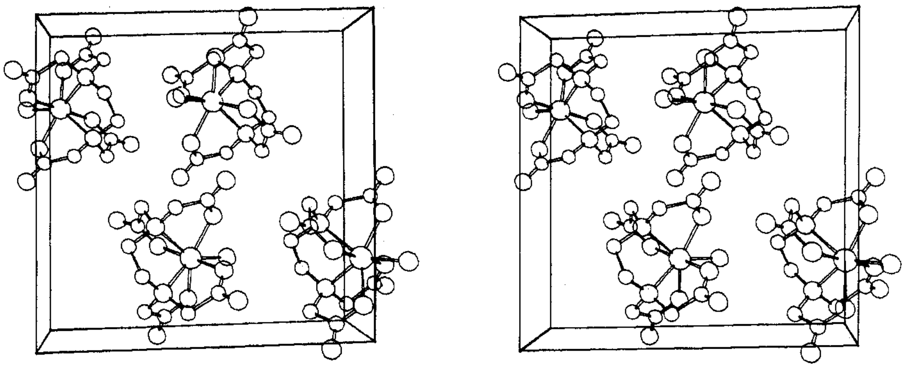

Figure 3.—Three-dimensional view of the crystal packing in a unit cell of $Sn^{IV}(OH_2)Y$ down the y axis. The x axis is vertical and the z axis is horizontal. The origin of the box is at 0,0,0.

W···O(4*) contacts are 2.734 ± 0.005 and 2.679 ± 0.005 Å, within the normal range for this type of interaction.[29] The hydrogen bonds appear to be fairly linear as indicated by O–H···O angles of 167 and 169°. Other details of the hydrogen-bonding geometry are given in Table VIII. The crystal contains no other close intermolecular contacts.

Anisotropic thermal motion appears to be most pronounced in the oxygen atom of the water molecule and in those carboxyl oxygens (O(2) and O(2*)) not involved in hydrogen bonding; the hydrogen-bonded pair O(4) and O(4*) also show fairly high anisotropy, however. Anisotropy decreases somewhat in the five-membered rings and especially at the nitrogen atoms, which act as bridgeheads between three rings: see Figure 1 and Table II. The isotropic temperature factors of the hydrogen atoms, which range between 0.5 and 4.8 Å^2, are subject to large errors because of the presence of the heavy atom.

Acknowledgment.—We thank P. P. North for kind assistance with the experimental work.

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The Crystal Structure of Tetraselenium Bis(hydrogen disulfate)

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A single-crystal X-ray diffraction study of the compound $Se_4(HS_2O_7)_2$, tetraselenium bis(hydrogen disulfate), shows that it crystallizes in the monoclinic space group $P2_1/c$, with the following unit cell dimensions: $a = 7.721$ (2), $b = 5.606$ (2), $c = 17.202$ (7) Å, $\beta = 109.78$ (2)°; density (measured) = 3.1 (1) g cm^{-3} and density (calculated) = 3.18 g cm^{-3} for $Z = 2$. A three-dimensional structure determination was based upon the 552 observed reflections measured on a quarter-circle GE diffractometer using Mo Kα radiation. Refinement by full-matrix least-squares methods of the parameters of all the atoms, except hydrogen, with anisotropic temperature factors, gave an unweighted R factor of 0.066. The Se_4^{2+} cation lies on a center of symmetry and is, within the accuracy of the experiment, strictly square planar, with Se–Se equal to 2.283 (4) Å. The anions are linked through hydrogen bonds into chains along the b axis. All the terminal S–O bonds are of the same length, 1.43 (2) Å, except the S–O(H) bond which is 1.56 (2) Å. The resultant asymmetry of the anion is reflected in an asymmetric bridge (S–O = 1.59 (2) and 1.67 (2) Å, S–O–S = 123 (1)°) and the deviations of the O–S–O angles from tetrahedral. These results are compared with the anion in $NO_2^+HS_2O_7^-$, for which a new refinement has been performed.

Introduction

The group VI elements, sulfur, selenium, and tellurium, dissolve in strong acids such as fluorosulfuric, sulfuric, and disulfuric acids to give intensely colored solutions. The results of cryoscopic, conductometric, and spectroscopic experiments on solutions of selenium in these solvents have shown the presence of the polyatomic cation Se_4^{2+}.[1] A number of compounds containing the Se_4^{2+} cation have been prepared and characterized by analytical and spectroscopic methods.[2] $Se_4^{2+}(HS_2O_7^-)_2$ was the first of these compounds to be prepared, and since it readily formed a well-defined crystalline solid, it was selected for an X-ray structure investigation. The purpose of the study was to demonstrate unambiguously the existence of the Se_4^{2+} cation and to determine its structure. A preliminary report has already appeared.[3]

Experimental Section

The preparation of the compound $Se_4(HS_2O_7)_2$ from selenium and 65% oleum has been described previously.[2] Slow crystallization from the viscous mother liquor yielded bright orange needle-

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[1] J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1968).

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