Stereochemistry of Tropolonato Complexes Utilizing the Higher Coordination Numbers. II. Tris(tropolonato)monochlorotin(IV) and Tris(tropolonato)monohydroxotin(IV)[1]

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Abstract: Seven-coordinate T_3SnCl and T_3SnOH molecules (T^- is $C_7H_5O_2^-$, the bidentate tropolonate ion) are isostructural in the dissimilar crystal structures observed for $T_3SnCl \cdot CHCl_3$ and $T_3SnOH \cdot (3 - 2x)H_2O \cdot xCH_3OH$ ($x \sim {}^1/_2$); both solvates, however, utilize two-molecule unit cells and the space group $P\bar{1}$. Measurement of lattice constants to <0.10% and of diffracted intensities by θ–2θ scanning employed Mo Kα radiation on Picker four-circle diffractometers. Intensity measurements were extended to $(\sin \theta)/\lambda = 0.65$ Å^{-1} for $T_3SnCl \cdot CHCl_3$, to 0.61 Å^{-1} for the T_3SnOH solvate; 4731 of 5488 and 3882 of 4192 recorded data from the respective crystals, statistically retained as observed, were used in the structure determinations. Substitutional disorder involving the CH_3OH and H_2O molecules in the structure of the T_3SnOH solvate did not prevent the direct placement of tropolonato hydrogen atoms nor the anisotropic refinement of structure to $R = 0.055$. Purely thermal disorder in $T_3SnCl \cdot CHCl_3$, concentrated in the $CHCl_3$ molecules, obscured all hydrogen positions and held R to 0.092. Six tropolonato oxygen atoms and the monodentate X (Cl or OH) ligand coordinate to the Sn(IV) atom in roughly pentagonal-bipyramidal geometry. Ligand X occupies an axial position, tropolonato ligand a spans an equatorial and the other axial position, while ligands b and c complete the quasi-pentagonal girdle around the Sn(IV) atom; C_s-m symmetry, with X, Sn, and ligand a lying in the mirror, is effectively observed. Apart from the lengths of the Sn–Cl (2.36 Å) and Sn–OH (1.97 Å) bonds, the two T_3SnX species are nearly isodimensional. The axial bond to tropolonato oxygen at 2.05–2.06 Å is ~0.10 Å shorter than the average for the five equatorial bonds. The most striking departures from pentagonal-bipyramidal geometry suggest a close structural affinity with the theoretically expected eight-coordinate SnT_4 molecule of the dodecahedral *mmmm* stereoisomeric type.

The genesis of our program to elucidate the crystalline and molecular structures of selected tropolonato complexes of the larger triply and quadruply charged cations is set forth in the introductory section of the accompanying paper[3] (I in this series). By reason of its low resultant charge and relatively small "bite" as a bidentate ligand, the tropolonate ion ($C_7H_5O_2^-$ or T^-), with the structural formula displayed in Figure 1, is especially well adapted to the formation of stable complexes that utilize the higher coordination numbers (>6).[4–6] A quantitative stereochemical description of the nine-coordinate tetrakis(tropolonato)-N,N′-dimethylformamidethorium(IV) molecule (hereinafter referred to as $DMFThT_4$) is presented in I;[3] structure determinations by three-dimensional X-ray methods for crystalline solvates of tris(tropolonato)monochlorotin(IV), T_3SnCl, and tris(tropolonato)monohydroxotin(IV), T_3SnOH, are reported at this time. The study of crystalline $T_3SnCl \cdot CHCl_3$, virtually completed and briefly reported[7] during 1967, provided some rather surprising results that, as outlined below, led to the study of the crystalline hydrate of T_3SnOH.

For a mononuclear seven-coordinate species that utilizes chemically identical monodentate ligands, three coordination polyhedra demand attention. Listed in order of increasing M–L/L–L, the ratio of complexing bond length to ligand packing diameter[3] in the "hard-sphere" model, these polyhedra are the C_{3v} monocapped octahedron, the C_{2v} monocapped trigonal prism, and the D_{5h} pentagonal bipyramid.[8] As indicated in Figure 1 of the accompanying paper,[3] the two monocapped polyhedra have only slightly different values of M–L/L–L; consequently, a physically realistic "softening" of the ligands or, otherwise put, a reasonable choice for neon-shell ligands of the Born repulsive exponent in the otherwise purely geometrical models yields ligand repulsive energies of comparable magnitudes for the two configurations.[9] The similar treatment of the pentagonal bipyramid,[9] for which the M–L/L–L value (0.850) is substantially larger (by ~0.05) than for the other polyhedra, yields a ligand repulsive energy comparable with that of the monocapped trigonal prism (and somewhat smaller than that of the monocapped octahedron) only for an improbably small Born exponent corresponding to unduly soft ligands. But going beyond these calculations, we note that hard-sphere geometry, which requires a uniform complexing bond length, is particularly unrealistic for the pentagonal-bipyramidal configuration. The two axial bonds can be and, indeed, are observed to be substantially shortened and presumably strengthened rela-

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(2) The author to whom correspondence should be addressed.

(3) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3626 (1970).

(4) (a) E. L. Muetterties and C. M. Wright, *ibid.*, **86**, 5132 (1964); (b) *ibid.*, **87**, 21 (1965); (c) *ibid.*, **87**, 4706 (1965); (d) *Quart. Rev.* (London), **21**, 109 (1967).

(5) (a) E. L. Muetterties, *J. Pure Appl. Chem.*, **10**, 54 (1965); (b) *J. Amer. Chem. Soc.*, **88**, 305 (1966).

(6) E. L. Muetterties, H. Roesky, and C. M. Wright, *ibid.*, **88**, 4856 (1966).

(7) J. J. Park, D. M. Collins, and J. L. Hoard, Summer Meeting of the American Crystallographic Association, Minneapolis, Minn., Aug 20–25, 1967, Abstract P13.

(8) The other seven-coordinate polyhedra mentioned by Muetterties and Wright[4d] are distorted versions with reduced symmetries of those cited herein. Such distortions may be required with chemically mixed and/or chelating ligands.

(9) (a) D. Britton, *Can. J. Chem.*, **38**, 818 (1960); (b) T. A. Claxton and G. C. Benson, *ibid.*, **44**, 157 (1966).

tive to the equatorial set while leaving the five close ligand contacts in the pentagonal girdle as the principal source of ligand repulsive energy. With no immediate prospect that the stereochemical preference of any seven-coordinate complex can be reliably predicted from fundamental electronic theory, the three distinctive geometries appear to have approximately equal *a priori* probabilities.

Just two mononuclear seven-coordinate species that utilize only monodentate ligands are known to be stable and to preserve configuration, more or less exactly, in various environments. The $TaF_7{}^{2-}$ ion exists as a monocapped trigonal-prismatic species in aqueous solution,[10] KF–LiF melts,[11] and the crystalline potassium salt.[12,13] The IF_7 molecule is a pentagonal-bipyramidal species,[17,18] but it is still uncertain whether the configuration of the ground state carries full D_{5h} symmetry.[9b,17a] Further, the coordination group around each metal atom in each of the binuclear $W_2Cl_9{}^{3-}$ and $Fe_2(CO)_9$ species[19] is of the monocapped octahedral type by reason of the metal–metal bonding.[20]

The two stereoisomeric forms of a seven-coordinate T_3SnCl or T_3SnOH molecule that seemingly require only minor alterations of the corresponding idealized coordination polyhedra place the monodentate ligand in the unique (capping) position of either the capped trigonal-prismatic or the monocapped octahedral configurations with accompanying chelation patterns that preserve the respective molecular symmetries of C_{2v} and C_3. Recent studies in other laboratories demonstrate, indeed, that both the tris(diphenylpropanedionato)aquoholmium(III)[22] and tris(1-phenyl-1,3-butanedionato)aquoyttrium(III)[23] molecules assume the capped octahedral configuration (albeit with a rather long bond in each case to the aquo ligand in the capping site).

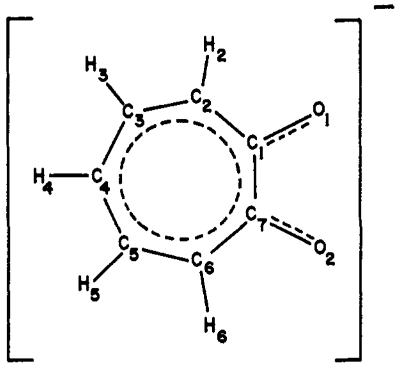

Figure 1. Diagram of the tropolonate ion (T^-) displaying the numbering scheme employed for the atoms. An additional literal subscript (a, b, or c) to the numbered atomic symbol is used to identify a particular tropolonato ligand within a T_3SnX molecule.

The coordination polyhedron of the T_3SnCl molecule, however, is clearly derived from the pentagonal bipyramid, with the molecular symmetry thereby limited to a single mirror plane. But having noted that the positioning of the chloro ligand on one of the axial sites of the bipyramidal group reduces the critical O···Cl nonbonding repulsions well below the minimum achievable with any other competing stereoisomer, it was conjectured that this steric factor might be responsible for stabilization of the T_3SnCl molecule in the observed configuration. The subsequent study of the corresponding hydroxo derivative was undertaken on the premise that O···OH nonbonding repulsions should play a rather less important role in determining configuration, thus allowing a wider freedom in the choice of configuration by the T_3SnOH molecule. The experimental fact is that the T_3SnCl and T_3SnOH molecules are isostructural in their differing crystalline environments. It is, however, of particular interest that the principal distortion from pentagonal-bipyramidal geometry, a feature of both species, is not calculated to minimize nonbonding repulsions, but is instead suggestive of a half-concealed preference for eight-coordination of the D_{2d} dodecahedral type.[24]

Experimental Section

A sample of T_3SnCl furnished by Dr. E. L. Muetterties was recrystallized from chloroform to give usable triclinic singlet crystals of the 1:1 solvate, $T_3SnCl \cdot CHCl_3$. Hydrated T_3SnOH was prepared as a fine powder following the general procedure of Muetterties and Wright;[4c] triclinic single crystals usable for structure determination were obtained by recrystallization from methanol. Weissenberg and precession photographs were employed to establish the space group as either P1 or $P\bar{1}$ for both of the (nonisomorphous) crystalline solvates and to determine preliminary sets of lattice constants; the choice of the centrosymmetric space group[25] ($P\bar{1}$), supported in both cases by the negative results of sensitive tests for piezoelectricity (using a Giebe–Scheibe detector designed by H. Diamant), was confirmed during the subsequent structure determinations and the detailed refinements thereof. A cell content of $2(T_3SnCl \cdot CHCl_3)$ led to fair agreement between the calculated density, 1.764 g/cc, and the experimental density, 1.78 g/cc, estimated by flotation of the somewhat soluble crystals in a C_2H_5I–CCl_4 mixture. The measured density, 1.65 g/cc, of the solvated T_3SnOH crystals was consistent with a cell content of $2(T_3SnOH \cdot 3H_2O)$, giving a calculated density of 1.657 g/cc, but it was equally consistent with a cell content of $2(T_3SnOH \cdot H_2O \cdot$

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(10) O. L. Keller, Jr., and A. Chetham-Strode, Jr., *Inorg. Chem.*, **5**, 367 (1966).

(11) J. S. Fordyce and R. L. Baum, *J. Chem. Phys.*, **44**, 1159 (1966).

(12) (a) J. L. Hoard, *J. Amer. Chem. Soc.*, **61**, 1252 (1939); (b) G. M. Brown and L. A. Walker, *Acta Crystallogr.*, **20**, 220 (1966).

(13) The $NbF_7{}^{2-}$ ion, isostructural and virtually isodimensional with $TaF_7{}^{2-}$, is stabilized in melts[14] and in crystalline K_2NbF_7,[12] but it is not a prominent species (because of partial hydrolysis) in aqueous solution.[15,16]

(14) J. S. Fordyce and R. L. Baum, *J. Chem. Phys.*, 44, 1166 (1966).

(15) O. L. Keller, Jr., *Inorg. Chem.*, **2**, 783 (1963).

(16) K. J. Packer and E. L. Muetterties, *J. Amer. Chem. Soc.*, **85**, 3035 (1963).

(17) (a) L. E. Bartell, private communication, 1969; (b) R. C. Lord, M. A. Lynch, Jr., W. C. Schumb, and E. J. Slowinski, Jr., *ibid.*, **72**, 522 (1950).

(18) R. D. Burbank and F. N. Bensey, *Acta Crystallogr.*, **15**, 1207 (1962), and references cited therein; (b) J. Donohue, *ibid.*, **18**, 1018 (1965).

(19) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 437, 441.

(20) Geometrical hybrids of the monocapped trigonal-prismatic and pentagonal-bipyramidal coordination groups are utilized in the seven-coordinate, sexadentate, monaquo complexes formed by high-spin Fe^{3+} and Mn^{2+} with the ethylenediaminetetraacetate ion.[21] The geometry of the Mn(II) complex approximates more closely to capped trigonal prismatic,[21a] that of the Fe(III) species even more closely to pentagonal bipyramidal.[21b] The analogous monaquoiron(III) complex formed with the 1,2-diaminocyclohexane-N,N′-tetraacetate ion has more nearly the capped trigonal-prismatic geometry.[21c] The capped octahedron is quite unsuited to such chelates.

(21) (a) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 3, 27 (1964); (b) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, 3, 34 (1964); (c) G. H. Cohen and J. L. Hoard, *J. Amer. Chem. Soc.*, **88**, 3288 (1966).

(22) A. Zalkin and D. H. Templeton, Summer Meeting of the American Crystallographic Association, Minneapolis, Minn., Aug 20–25, 1967, Abstract T7.

(23) F. A. Cotton and P. Legzdino, *Inorg. Chem.*, 7, 1777 (1968).

(24) J. L. Hoard and J. V. Silverton, *ibid.*, **2**, 235 (1963).

(25) "International Tables for X-Ray Crystallography," Vol. I, "Symmetry Groups," The Kynoch Press, Birmingham, England, 1952, p 75.

CH_3OH), with a calculated density of 1.654 g/cc; the subsequent structure determination suggested that a partial substitution of methanol for loosely held water, with each molecule of methanol replacing a contiguous pair of water molecules, had occurred during recrystallization to give the crystals a composition, $T_3SnOH \cdot (3 - 2x)H_2O \cdot xCH_3OH$, with $0.40 < x \lesssim 0.5$. This minor disorder in the crystalline arrangement had no significant effect on the determination of the structural parameters of the T_3SnOH molecule (*vide infra*).

Crystal specimens used for the collection of quantitative intensity data approximated in form to rectangular parallelepipeds, 0.17 × 0.08 × 0.05 and 0.25 × 0.12 × 0.10 mm for the respective chloro and hydroxo compounds; each specimen was mounted with its longest dimension nearly parallel to the principal axis of the goniometer head. All measurements were carried out on Picker four-circle diffractometers with Zr-filtered Mo Kα radiation at an ambient laboratory temperature of 21 ± 1°. Following the precise centering of a specimen, 25 reflections representing a good sampling of reciprocal space and instrument settings were used to align the crystal and determine precise lattice constants as a basis for calculating angular settings for the recording of intensity data. Least-squares refinement[26] of the diffraction geometry of these reflections led to the following precise lattice constants (λ 0.71069 Å): for $T_3SnCl \cdot CHCl_3$, $a = 10.898$ (5), $b = 12.175$ (6), $c = 9.462$ (5) Å, $\cos \alpha = 0.2964$ (2) or $\alpha = 72.75$, $\cos \beta = 0.0120$ (1) or $\beta = 89.31$, and $\cos \gamma = 0.0084$ (2) or $\gamma = 89.52°$;[27] for $T_3SnOH \cdot (3 - 2x)H_2O \cdot xCH_3OH$, $a = 12.038$ (10), $b = 10.145$ (8), $c = 10.101$. (10) Å, $\cos \alpha = -0.3863$ or $\alpha = 112.73$, $\cos \beta = -0.1079$ (5) or $\beta = 96.20$, and $\cos \gamma = 0.1452$ (4) or $\gamma = 98.35°$.

The measurement of diffracted intensities from the $T_3SnCl \cdot CHCl_3$ crystal employed θ–2θ scans on a card-controlled diffractometer. Each scan (1°/min) included a variable increment in angle above the 2.2° minimum to allow for spectral dispersion; background counts each of 40 sec duration were taken at both limits of the scan. The data were recorded in ten concentric shells of sequentially larger scattering angle, and all of the 5488 independent reflections having $(\sin \theta)/\lambda \lesssim 0.65$ (the theoretical Cu Kα limiting sphere) were examined. Ten standard reflections that were well distributed in reciprocal space were used for periodic checking on the alignment and possible deterioration of the crystal; no significant alterations in the standard intensities were observed during the course of the measurements. The procedure of intensity measurement for the solvated T_3SnOH crystal followed the same pattern except that all angular settings were manual. The data, recorded in concentric shells of increasing $(\sin \theta)/\lambda$, were quite satisfactorily reproducible during examination of the inner 4028 independent reflections. At this point the crystal split, apparently spontaneously, with loss of approximately half of the original. Realignment of the fragment adhering to the fiber allowed the examination of an additional 164 reflections before it too separated from the fiber. No attempt was made to extend the intensity measurements with another specimen to higher scattering angles because (1) the manual diffractometer was scheduled for conversion to computer-controlled operation, (2) the 4192 reflections already measured comprised ~80% of those within the Cu Kα limiting sphere, and (3) the isostructural relation between the T_3SnCl and the T_3SnOH molecules soon became apparent.

With the cited dimensions and mounting of the $T_3SnCl \cdot CHCl_3$ crystal, a linear absorption coefficient for Mo Kα radiation of 1.6 mm^{-1}, and the technique of intensity measurement described above, the maximum error from neglect of absorption corrections was calculated to be <4% in any intensity or <2% in any amplitude. Absorption was even less important in the solvated T_3SnOH crystal; consequently, no corrections were applied to either data set. The measured net intensities (counts sec^{-1}) were then reduced to relative squared amplitudes, $|F_o|^2$, through application of the Lorentz and polarization factor (Lp) appropriate to the equatorial geometry of measurement. Rejection as objectively unobserved of those data for which $|F_o| < 0.5\sigma(|F_o|)$, wherein $\sigma(|F_o|)$ is the standard deviation computed from $\sigma^2(|F_o|) = (C_t + k^2B)/4|F_o|^2Lp^2$, C_t being the total count from the scan, k the ratio of scanning time to total background counting time, and B the total background count, left 4731 and 3882 independent observed reflections in the respective $T_3SnCl \cdot CHCl_3$ and $T_3SnOH \cdot (3 - 2x)H_2O \cdot xCH_3OH$ data sets for the determination of the crystalline arrangements.

The approximate structures of both crystals were readily developed by applying the heavy-atom technique in Patterson syntheses of the $|F_o|^2$ data followed by Fourier and difference syntheses of the structure amplitudes; the lower angle data, amounting to little more than the reflections lying within the chromium Kα sphere, were employed at this stage. Both structures were then subjected to full-matrix least-squares refinement[28, 29] using all of the amplitude data and individual isotropic thermal parameters for the several atoms. Fully anisotropic refinement of the structural parameters, as carried out on the IBM 360/65 computer, utilized the block-diagonal least-squares program described in the accompanying paper[3] (see footnote 19 therein).[30] Values of the conventional unweighted residual (R) obtained upon convergence were 0.092 for the 4731 $T_3SnCl \cdot CHCl_3$ data and 0.064 for the 3882 data from the solvated T_3SnOH crystal. A Fourier difference synthesis of these latter data then disclosed the approximate positions of 18 hydrogen atoms in the asymmetric unit of structure (including all of those in the T_3SnOH molecule) and, in addition, two minor peaks with the maximum densities of 2.2 and 2.6 electrons Å^{-3}. These peaks were readily interpretable (see Table X and the associated discussion) as arising from a fractional occupancy, x, of the first position by methyl carbons (C_{Me}) of methanol and the correlated fractional occupancy, $1 - x$, of the second position by water molecules (W_3); an x approaching, but not exceeding, $^1/_2$ was consistent with the data. The inclusion of contributions from these peaks and from the hydrogen atoms, all with isotropic thermal parameters, in the otherwise anisotropic refinement had no objectively significant effect on the parameters of the fully established atoms in the crystalline arrangement, but did lower R to a final value of 0.055.

A final difference synthesis of the $T_3SnCl \cdot CHCl_3$ data, by contrast, gave no reliable indications of hydrogen positions, nor did it exhibit any uninterpretable peak of magnitude greater than 0.8 electron Å^{-3}. This evidence against any significant positional disorder or vacancies in the crystalline arrangement was in full agreement with the density measurements and with the results of an earlier introduction into the refinement of a variable occupancy factor for the chloroform molecule. Both the large R of 0.092 and the lack of direct evidence for hydrogen positions were attributable to the extraordinarily large and complex thermal motions of the heavily scattering chloroform molecules—motions that, at best, were rather inadequately described by the model. The equivalent isotropic thermal parameters of 12–13 Å^2 obtained for the three chlorine atoms in the chloroform molecule were more than twice the averaged value of B for the tropolonato carbon atoms within the T_3SnCl molecule. The thermal motions of the chlorine atoms in the chloroform molecule, extraordinarily anisotropic (as seen from Table II and Figure 2), were particularly suggestive of highly excited libration of the molecule about its principal axis. Concomitant with the unduly large movement of the chloroform molecule, the T_3SnCl molecule was seen to carry thermal parameters that were substantially larger, on the average, than those which characterized the T_3SnOH molecule in its own crystalline environment.

The atomic coordinates and thermal parameters of the $T_3SnCl \cdot CHCl_3$ structure are listed in Tables I and II, respectively; corresponding data for the solvated T_3SnOH crystalline arrangement are given in Tables III–V.[31]

Discussion of Results

Models in perspective of the T_3SnCl and T_3SnOH molecules, hydrogen atoms omitted, are shown on

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(26) Use was made of the PICK II computer program, a revision in this laboratory of W. C. Hamilton's MODE I program.

(27) The transformation of axes, $\vec{a}' = -\vec{a}$, $\vec{b}' = -\vec{b}$, $\vec{c}' = \vec{c}$, gives the more conventional set of angles, $\alpha' = 107.25$, $\beta' = 90.69$, and $\gamma' = 89.52°$.

(28) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(29) Atomic form factors were from D. T. Cromer and J. T. Waber, *Acta Crystallogr., Sect. A*, **24** 321 (1968). Corrections, real and imaginary, for the anomalous scattering of the tin and the chlorine atoms were from D. T. Cromer, *ibid.*, **18**, 17 (1965).

(30) A further definitive test, with highly satisfactory results, of this block-diagonal least-squares program is reported in D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3761 (1970).

(31) Tables of observed and calculated amplitudes from these refinements have been deposited as Document No. NAPS-00874 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and remitting \$3.00 for photoprints or \$1.00 for microfiche. Advance payment is required. Make checks or money orders payable to ASIS–NAPS.

Table I. Atomic Coordinates in Crystalline $T_3SnCl \cdot CHCl_3$[a]

Atom type[b]	Coordinates 10^4x	 10^4y	 10^4z
Cl	8887 (3)	6958 (3)	−920 (4)
O_{a1}	5406 (6)	8517 (5)	−36 (7)
O_{a2}	5981 (6)	6360 (5)	524 (7)
O_{b1}	7141 (6)	9272 (5)	−2449 (7)
O_{b2}	6246 (7)	7294 (6)	−2224 (8)
O_{c1}	7965 (7)	9213 (6)	65 (7)
O_{c2}	7499 (7)	7242 (5)	1849 (8)
C_{a1}	4534 (10)	7786 (9)	505 (10)
C_{a2}	3409 (10)	8249 (10)	806 (12)
C_{a3}	2311 (13)	7687 (12)	1345 (15)
C_{a4}	2038 (12)	6545 (12)	1695 (14)
C_{a5}	2823 (11)	5616 (9)	1696 (11)
C_{a6}	4059 (9)	5620 (8)	1322 (10)
C_{a7}	4874 (9)	6564 (8)	800 (10)
C_{b1}	6729 (9)	9125 (8)	−3645 (10)
C_{b2}	6797 (10)	10079 (9)	−4944 (12)
C_{b3}	6372 (10)	10176 (10)	−6378 (12)
C_{b4}	5805 (10)	9365 (11)	−6916 (12)
C_{b5}	5512 (11)	8227 (11)	−6130 (12)
C_{b6}	5712 (11)	7640 (10)	−4658 (12)
C_{b7}	6228 (9)	8008 (8)	−3534 (10)
C_{c1}	8495 (9)	8980 (9)	1326 (11)
C_{c2}	9246 (10)	9844 (11)	1584 (13)
C_{c3}	9962 (11)	9800 (13)	2808 (13)
C_{c4}	10056 (13)	8931 (13)	4161 (15)
C_{c5}	9428 (12)	7897 (12)	4609 (15)
C_{c6}	8640 (12)	7423 (11)	3820 (13)
C_{c7}	8238 (10)	7867 (10)	2347 (12)
Cl_{s1}	7358 (8)	3254 (5)	2506 (7)
Cl_{s2}	9169 (5)	4688 (5)	3198 (11)
Cl_{s3}	6800 (8)	4520 (6)	4481 (7)
C_s	7622 (14)	4537 (13)	2894 (17)
Sn	10^5x = 70528 (6)	10^5y = 78571 (6)	10^5z = −4822 (7)

[a] Figures in parentheses are the estimated standard deviations. [b]Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the particular ligand (a, b, or c), and a numerical subscript that follows the numbering scheme given in Figure 1 for the tropolonate ion.

slightly different scales in Figures 2 and 3, respectively; each atom is represented by an ellipsoid having the shape, orientation, and relative size concomitant with the thermal parameters listed in Tables II and V. Although the two crystalline arrangements are markedly different, the T_3SnCl and T_3SnOH molecules are essentially isostructural. Six tropolonato oxygen atoms and the monodentate X (Cl or OH) ligand are coordinated to the tin(IV) atom in fair approximation to pentagonal-bipyramidal geometry. Ligand X takes one axial position, tropolonato ligand a spans an equatorial and the second axial position, while tropolonato ligands b and c complete the equatorial girdle around the Sn(IV) atom. The maximum permissible symmetry of this molecular configuration is C_s-m, with the Sn(IV) atom, ligand X, and tropolonato ligand a lying in the mirror plane, and with tropolonato ligands b and c rendered structurally equivalent by reflection through this plane. The deviations observed in the crystals from C_s symmetry, not large for either the T_3SnCl or the T_3SnOH molecule, seem to be ascribable to packing constraints.

The adoption of a simple, but specific, numbering scheme for the atoms in the common molecular configuration expedites the more detailed treatment of the structural characteristics of the T_3SnCl and T_3SnOH species. Thus the symbol for each atom of a tropolonato ligand usually will carry both a literal subscript to identify the particular ligand (a, b, or c) and a numerical

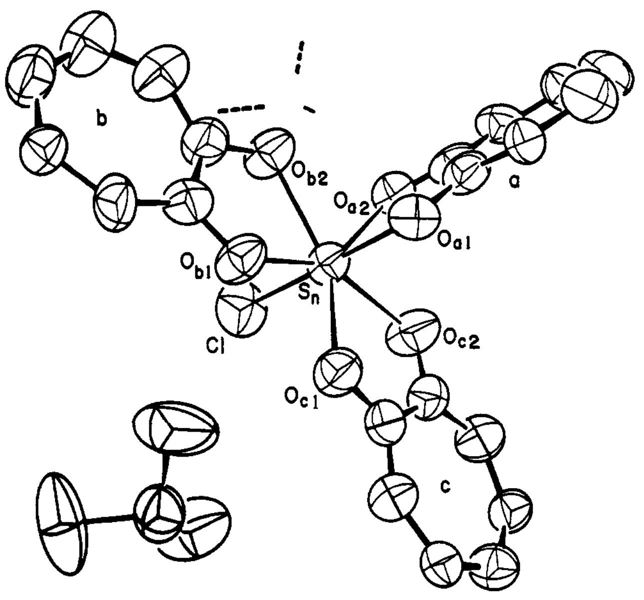

Figure 2. Models in perspective of the T_3SnCl and chloroform molecules. The dotted lines indicate the relative positioning in the crystal of the $CHCl_3$ molecule that lies nearest to a T_3SnCl complex.

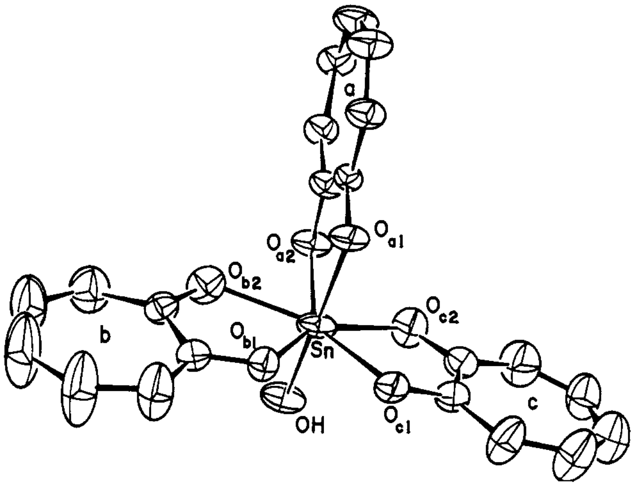

Figure 3. Model in perspective of the T_3SnOH molecule reduced in scale by ~15% from that of the T_3SnCl molecule in Figure 2.

subscript that follows the pattern given in Figure 1 for the tropolonate ion; additionally, the numbering patterns for ligands b and c observe the mirroring operation that presumably requires their symmetry equivalence in the free molecule.

Calculation by least-squares fitting of the mean plane for the nine atoms of each C_7O_2 tropolonato skeleton in both molecules shows that only tropolonato skeleton a in the T_3SnCl molecule departs significantly from planarity. This distortion, however, seems to have structural significance only in respect to the crystal packing; oxygen atoms O_{a1} and O_{a2} are displaced −0.06 and 0.05 Å, respectively, from the mean plane, while the carbon atoms are limited to apparent displacements of $\lesssim 0.04$ Å. The principal component of this distortion resides in a slight twisting of the skeleton about its unique (quasi-twofold) axis, *i.e.*, about the line passing through the C_4 atom and the midpoint of the C_1–C_7 bond (see Figure 1).

Table II. Thermal Parameters in Crystalline $T_3SnCl \cdot CHCl_3$[a]

Atom type[c]	Anisotropic parameters, Å²						
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[b] Å²
Sn	4.55 (8)	3.26 (2)	3.71 (3)	−0.19 (2)	−0.51 (2)	−1.03 (2)	3.77
Cl	5.9 (2)	7.3 (2)	7.9 (1)	1.2 (1)	0.2 (1)	−3.2 (2)	6.6
O_{a1}	5.0 (3)	3.3 (3)	4.9 (3)	0.5 (2)	0.0 (3)	−1.3 (2)	4.3
O_{a2}	5.3 (3)	3.3 (3)	4.4 (3)	−0.1 (2)	−0.4 (3)	−1.2 (2)	4.2
O_{b1}	5.4 (3)	3.8 (3)	3.9 (3)	−1.0 (3)	−0.7 (2)	−0.6 (2)	4.3
O_{b2}	7.8 (5)	4.1 (3)	4.0 (3)	−1.6 (3)	−0.8 (3)	−1.0 (3)	4.9
O_{c1}	6.2 (4)	4.0 (3)	4.2 (3)	−0.6 (3)	−1.1 (3)	−1.6 (2)	4.4
O_{c2}	6.7 (4)	3.8 (3)	4.4 (3)	0.3 (3)	−1.4 (3)	−1.0 (3)	4.7
C_{a1}	5.4 (5)	4.5 (5)	3.7 (4)	−0.3 (4)	−0.9 (4)	−1.2 (3)	4.4
C_{a2}	4.4 (5)	6.7 (6)	4.5 (5)	0.7 (4)	−0.2 (4)	−1.5 (4)	5.1
C_{a3}	6.9 (7)	7.1 (8)	6.4 (7)	0.3 (6)	1.3 (6)	−1.6 (6)	6.8
C_{a4}	5.8 (7)	9.1 (9)	6.8 (7)	−0.2 (6)	1.8 (6)	−0.9 (7)	7.1
C_{a5}	6.2 (7)	8.3 (8)	6.1 (6)	−2.5 (6)	1.4 (5)	−2.3 (6)	6.4
C_{a6}	6.3 (6)	4.6 (5)	4.4 (5)	−1.2 (4)	0.3 (4)	−1.3 (4)	5.0
C_{a7}	5.6 (5)	3.7 (4)	3.1 (4)	−0.3 (3)	−0.9 (3)	−1.2 (3)	3.8
C_{b1}	4.3 (4)	4.3 (4)	3.7 (4)	0.0 (3)	−0.1 (3)	−1.2 (3)	4.1
C_{b2}	4.8 (5)	5.1 (5)	4.5 (5)	0.1 (4)	−0.3 (4)	−0.8 (4)	4.9
C_{b3}	4.5 (5)	6.4 (6)	4.6 (5)	0.7 (4)	0.1 (4)	−1.2 (4)	5.1
C_{b4}	5.1 (5)	7.2 (7)	4.1 (5)	0.5 (5)	0.2 (4)	−1.6 (5)	5.3
C_{b5}	5.1 (6)	7.8 (7)	4.6 (5)	0.0 (5)	−0.1 (4)	−2.9 (5)	5.3
C_{b6}	6.6 (6)	5.7 (6)	4.2 (5)	0.2 (5)	−0.1 (4)	−2.4 (4)	5.1
C_{b7}	4.3 (4)	4.5 (5)	4.0 (4)	−0.3 (3)	−0.3 (3)	−1.3 (4)	4.2
C_{c1}	4.6 (5)	4.9 (5)	4.7 (5)	0.1 (4)	0.2 (4)	−2.2 (4)	4.5
C_{c2}	4.4 (5)	7.9 (7)	6.4 (6)	−0.9 (5)	−0.3 (4)	−4.1 (6)	5.3
C_{c3}	5.3 (6)	9.7 (9)	5.7 (6)	−1.6 (6)	0.0 (5)	−4.1 (6)	5.9
C_{c4}	4.9 (6)	10.0 (9)	6.8 (7)	0.7 (6)	−1.9 (5)	−4.1 (7)	6.3
C_{c5}	6.7 (7)	6.8 (7)	7.4 (7)	1.6 (6)	−2.5 (6)	−3.0 (6)	6.4
C_{c6}	7.4 (7)	5.9 (6)	5.2 (6)	1.4 (5)	−1.7 (5)	−2.1 (5)	5.8
C_{c7}	4.6 (5)	5.6 (5)	4.7 (5)	0.0 (4)	−0.4 (4)	−1.7 (4)	4.9
Cl_{s1}	23.3 (7)	8.7 (3)	10.7 (4)	−3.4 (4)	−1.6 (4)	−3.3 (3)	12.4
Cl_{s2}	8.1 (3)	8.6 (3)	30.7 (9)	1.4 (2)	−3.4 (4)	−2.8 (4)	12.9
Cl_{s3}	21.8 (7)	16.1 (5)	10.7 (4)	−10.3 (5)	5.6 (4)	−6.0 (4)	13.0
C_s	7.6 (5)	7.0 (8)	8.1 (9)	−0.8 (6)	−0.9 (7)	−1.2 (7)	7.6

[a] The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. The B_{ij}'s in Å² are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$. [b] Isotropic thermal parameter calculated from $B = 4[V^2 \cdot \det(\beta_{ij})]^{1/3}$. [c] Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the particular ligand (a, b, or c), and a numerical subscript that follows the numbering scheme given in Figure 1 for the tropolonate ion.

The most striking departures from C_s symmetry in the molecular conformations arise from foldings of the five-membered chelate rings (-Sn-O-C-C-O-) along the edges (O···O) of the coordination polyhedra. Thus the angle of folding at the polyhedron edge between the mean plane of the tropolonato skeleton and the plane defined by the tin and the two oxygen atoms takes a distinctive value for each of the tropolonato ligands in both molecules; namely, 5.3, 0.4, and 11.0° in a, b, and c, respectively, of T_3SnCl, and 2.7, 1.0, and 7.0° in a, b, and c, respectively, of T_3SnOH. The accompanying displacement of the Sn(IV) atom from the mean plane of the tropolonato skeleton ranges from 0.02 Å for the minimum folding of 0.4° to 0.33 Å for the maximum folding of 11.0°. This largest folding is only about half that (23.4°) observed for one of the four tropolonato skeletons in the $DMFThT_4$ molecule.[3]

Looking now at the stereochemical parameters of the coordination groups given in Tables VI and VII, it is clear that the T_3SnCl and T_3SnOH molecules exhibit very similar patterns of complexing Sn-O bond lengths (Table VI) and of all bond angles (Table VII). Axial bonds (Figures 2 and 3) are substantially shorter, while all equatorial bonds appear to be somewhat longer, than the values anticipated for Sn(IV) in octahedral six-coordination (2.11 Å for Sn-O and 2.44 Å for Sn-Cl[32]). The axial bond to tropolonato oxygen (Sn-O_{a1}) in each molecule is ∼0.10 Å shorter than the averaged length of the five equatorial bonds.[33] The notably short Sn-OH bond (1.974 Å) bespeaks especially strong complexing. Neither of the T_3SnX species displays measurable electrolytic dissociation in solution.[4a,c]

The pentagonal girdle in each molecule carries five very tight O···O contacts that, in T_3SnCl, average to 2.534 Å and in T_3SnOH to 2.552 Å, some 0.25–0.27 Å below the van der Waals diameter (2.80 Å) of oxygen. Two of these contacts in each molecule represent the normal "bite" of the tropolonato ligand, as independently evaluated in the loosely packed $DMFThT_4$ molecule,[3] and are to be ignored in considering the nonbonding repulsive energy. Inasmuch as this energy increases exponentially with decreasing separation, one sees that the equatorial bonds have already absorbed a substantial destabilizing energy associated with the three short O···O inter-ring contacts, and that a reduction of 0.10 Å in the bond length (to make it comparable with the axial value) is incompatible with stability for the molecular configuration.

A molecular orbital treatment by Oakland and Duffey[35a] of σ bonding in the IF_7 molecule suggests

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(32) See ref 19, Chapter 7.

(33) The observed difference of −0.014 Å between the averaged Sn-O bond lengths in the respective T_3SnOH and T_3SnCl molecules is perhaps more apparent than real. Corrections to these bond lengths for partially correlated motions in the crystals are necessarily positive[34] and are expected to be larger for the $T_3SnCl \cdot CHCl_3$ structure with the thermal parameters listed in Table II.

(34) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

(35) (a) R. L. Oakland and G. H. Duffey, *J. Chem. Phys.*, **46**, 19 (1967); (b) see also G. H. Duffey, *ibid.*, **18**, 943 (1950).

Table III. Atomic Coordinates in Crystalline $T_3SnOH \cdot (3 - 2x)H_2O \cdot xCH_3OH$[a]

Atom type[b]	Coordinates 10^4x	 10^4y	 10^4z
OH	4078 (5)	3366 (6)	4807 (7)
O_{a1}	1444 (4)	301 (5)	4579 (6)
O_{a2}	3599 (4)	228 (6)	4700 (7)
O_{b1}	1544 (5)	2377 (6)	3253 (6)
O_{b2}	2937 (5)	696 (7)	2444 (7)
O_{c1}	1849 (5)	3480 (6)	5997 (6)
O_{c2}	3338 (5)	2415 (7)	7006 (7)
C_{a1}	1745 (6)	−879 (7)	4641 (8)
C_{a2}	897 (7)	−1931 (8)	4665 (10)
C_{a3}	947 (8)	−3259 (9)	4725 (11)
C_{a4}	1864 (8)	−3913 (9)	4763 (12)
C_{a5}	2986 (8)	−3372 (9)	4755 (11)
C_{a6}	3465 (7)	−2038 (8)	4746 (9)
C_{a7}	2959 (6)	−891 (7)	4697 (9)
C_{b1}	1535 (7)	1806 (9)	1870 (9)
C_{b2}	791 (10)	2135 (13)	925 (11)
C_{b3}	584 (11)	1623 (15)	−561 (12)
C_{b4}	1080 (10)	700 (14)	−1616 (11)
C_{b5}	1930 (10)	15 (13)	−1345 (11)
C_{b6}	2480 (9)	64 (12)	−40 (11)
C_{b7}	2335 (7)	838 (9)	1410 (9)
C_{c1}	2155 (7)	4047 (9)	7396 (9)
C_{c2}	1663 (11)	5198 (14)	8203 (12)
C_{c3}	1807 (15)	5978 (18)	9691 (13)
C_{c4}	2491 (16)	5847 (18)	10789 (13)
C_{c5}	3237 (13)	4905 (16)	10664 (13)
C_{c6}	3451 (10)	3888 (12)	9438 (12)
C_{c7}	3016 (7)	3444 (9)	7978 (9)
O_3[c]	4966 (7)	4058 (8)	2792 (8)
W_2[d]	4986 (7)	771 (10)	7992 (9)
W_3[d,e]	5519 (16)	1605 (22)	1012 (21)
C_{Me}[f]	5469 (20)	2887 (27)	1866 (26)
Sn	10^5x = 27311 (4)	10^5y = 19283 (3)	10^5z = 46794 (6)

[a] Figures in parentheses are the estimated standard deviations. [b] Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the particular ligand (a, b, or c), and a numerical subscript that follows the numbering scheme given in Figure 1 for the tropolonate ion. [c] Includes xOH and $(1 - x)H_2O$ with $x \sim 1/2$; see Discussion. [d] Symbols used for water molecules. [e] Occupancy factor of $1 - x \sim 1/2$; see Discussion. [f] Methyl carbon of CH_3OH with occupancy factor of $x \sim 1/2$; see Discussion.

Table IV. Approximate Parameters of Hydrogen Atoms in $T_3SnOH \cdot (3 - 2x)H_2O \cdot xCH_3OH$[a]

Atom type	Coordinates 10^3x	 10^3y	 10^3z	Isotropic thermal parameter B, Å^2
H_{a2}	5 (7)	−176 (9)	469 (9)	1 (2)
H_{a3}	26 (7)	−377 (9)	483 (9)	1 (2)
H_{a4}	190 (9)	−466 (12)	519 (12)	4 (3)
H_{a5}	344 (13)	−440 (16)	485 (12)	7 (4)
H_{a6}	415 (9)	−184 (12)	446 (12)	4 (3)
H_{b2}	46 (10)	236 (13)	142 (13)	5 (3)
H_{b3}	0 (11)	201 (14)	−124 (14)	7 (3)
H_{b4}	78 (12)	75 (15)	−259 (16)	7 (4)
H_{b5}	237 (15)	−17 (19)	−213 (19)	9 (5)
H_{b6}	308 (9)	−47 (12)	−3 (12)	2 (3)
H_{c2}	112 (10)	532 (13)	740 (13)	4 (3)
H_{c3}	119 (12)	677 (14)	964 (15)	8 (4)
H_{c4}	266 (14)	640 (18)	1133 (18)	11 (5)
H_{c5}	376 (9)	505 (11)	1161 (11)	3 (2)
H_{c6}	382 (8)	340 (10)	956 (10)	1 (2)
H_{OH}[b]	481 (13)	388 (16)	595 (16)	13 (4)
H_{O_3}[c]	428 (9)	412 (12)	368 (12)	9 (3)
H_{W_2}[c]	583 (12)	81 (15)	798 (15)	9 (4)

[a] Figures in parentheses are the estimated standard deviations. [b] Hydrogen atom of the hydroxo ligand. [c] Hydrogen atoms in water molecules.

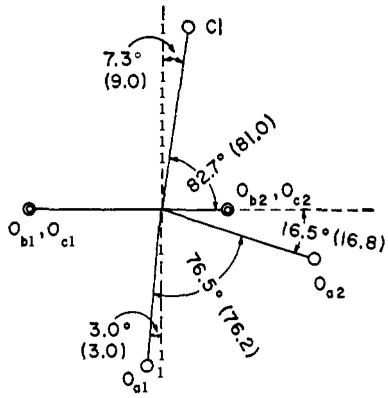

Figure 4. Diagram of the T_3SnX coordination group in projection on the quasi-mirror plane. Angles of rotation of Sn–X and Sn–O bonds from the quasi-fivefold axis or the equatorial plane are given for both the T_3SnCl and (in parentheses) T_3SnOH molecules.

stability of the D_{5h} pentagonal-bipyramidal configuration relative to C_{3v} monocapped octahedral geometry; the more pertinent comparison with the C_{2v} capped trigonal-prismatic stereochemistry displayed by the stable TaF_7^{2-} species was not made. The calculated charge distribution in the D_{5h} species lends a substantial ionic character to the complexing bonds; it attributes very little of the bonding electron density to the three 5d I(VII) orbitals employed in σ bonding, but puts it rather in the $5sp^3$ orbitals. In contrast with I(VII) and Sn(IV), the d orbitals of total quantum number $n - 1$ in the valence shells of Ta(V), Nb(V), etc., may be used for complexing with equal or greater advantage than the nsp^3 orbitals. With this reversal in the relative stabilities of the d and sp^3 sets of valence shell orbitals (and with π bonding also to be considered), there is little reason to anticipate that B subgroup and transition elements in their highest oxidation states will exhibit the same stereochemical preferences.

The tin and four of the five oxygen atoms (O_{b1}, O_{b2}, O_{c1}, O_{c2}) of the pentagonal girdle are nearly coplanar in both molecules (displacements ≤ 0.03 Å). The equatorial plane thus defined is virtually perpendicular to the mean plane defined by the Sn–X, Sn–O_{a1}, and Sn–O_{a2} bonds—to, that is, the observed quasi-mirror plane of the coordination group. Figure 4, a projection of the coordination group onto the quasi-mirror plane, shows that the Sn–X, Sn–O_{a1}, and Sn–O_{a2} bonds have undergone a clockwise rotation around the plane normal from the orientations that correspond to ideal pentagonal-bipyramidal geometry. The Sn–O_{a2} bond is rotated out of the equatorial plane by 16.5 or by 16.8° in the respective T_3SnCl and T_3SnOH molecules, and both the Sn–X and Sn–O_{a1} bonds are rotated off the quasi-fivefold axis through the angles entered on Figure 4.

As a consequence of the rotation of the Sn–X bond from the quasi-fivefold axis, the $X \cdots O_{b1}$ and $X \cdots O_{c1}$ packing distances are increased, while the $X \cdots O_{b2}$ and $X \cdots O_{c2}$ are decreased. Averaged distances of each class become $Cl \cdots O_1$, 3.222; $Cl \cdots O_2$, 3.118; $OH \cdots O_1$, 3.104; $OH \cdots O_2$, 2.883 Å. The averaged $Cl \cdots O_2$ separation is 0.08 Å less than the sum of the van der Waals radii, and the $OH \cdots O_2$ separation is only 0.08 Å larger than the van der Waals diameter of oxygen. From a purely steric point of view, the off-axis positioning of the

Table V. Thermal Parameters in Crystalline $T_3SnOH\cdot(3-2x)H_2O\cdot xCH_3OH$[a]

	Anisotropic parameters, Å²						
Atom type[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[c] Å²
Sn	2.14 (2)	2.12 (2)	3.83 (2)	0.97 (2)	0.75 (2)	1.48 (2)	2.3
OH	3.2 (3)	2.9 (3)	6.0 (3)	0.2 (2)	1.4 (2)	2.1 (2)	3.6
O_{a1}	2.1 (2)	2.3 (2)	5.3 (3)	1.1 (2)	0.9 (2)	2.3 (2)	2.4
O_{a2}	2.0 (2)	2.6 (2)	5.5 (3)	1.1 (2)	0.7 (2)	2.2 (2)	2.7
O_{b1}	3.7 (3)	3.1 (2)	3.6 (3)	2.1 (2)	0.9 (2)	1.3 (2)	3.0
O_{b2}	4.2 (3)	4.4 (3)	3.8 (3)	2.4 (2)	1.0 (2)	1.5 (2)	3.8
O_{c1}	3.1 (2)	3.4 (2)	3.1 (2)	1.9 (2)	0.5 (2)	1.3 (2)	2.9
O_{c2}	3.9 (3)	4.2 (3)	4.6 (3)	2.0 (2)	1.0 (2)	2.3 (2)	3.8
C_{a1}	2.6 (3)	1.6 (3)	3.0 (3)	0.9 (2)	0.3 (2)	0.9 (2)	2.2
C_{a2}	2.6 (3)	2.6 (3)	4.8 (4)	0.9 (3)	0.7 (3)	1.8 (3)	3.0
C_{a3}	3.4 (4)	3.1 (4)	6.1 (5)	0.7 (3)	0.9 (4)	2.6 (4)	3.7
C_{a4}	4.2 (4)	2.5 (3)	6.7 (6)	1.0 (3)	0.4 (4)	2.6 (4)	3.6
C_{a5}	4.4 (4)	2.6 (3)	5.2 (5)	1.7 (3)	0.4 (3)	1.9 (3)	3.4
C_{a6}	2.7 (3)	2.9 (3)	4.1 (4)	1.4 (3)	0.3 (3)	1.6 (3)	2.8
C_{a7}	2.6 (3)	2.1 (3)	3.6 (3)	1.1 (2)	0.4 (3)	1.3 (3)	2.4
C_{b1}	3.1 (3)	3.1 (3)	3.7 (4)	1.1 (3)	0.9 (3)	1.5 (3)	3.2
C_{b2}	6.0 (6)	6.7 (6)	3.8 (4)	3.5 (5)	1.2 (4)	2.5 (4)	4.7
C_{b3}	7.0 (7)	8.6 (8)	4.4 (5)	3.6 (6)	1.3 (5)	3.2 (5)	5.8
C_{b4}	5.7 (6)	7.8 (7)	3.3 (4)	2.0 (5)	1.0 (4)	1.9 (5)	5.3
C_{b5}	6.2 (6)	6.1 (6)	3.6 (4)	2.0 (5)	1.5 (4)	1.2 (4)	5.2
C_{b6}	5.0 (5)	5.3 (5)	4.2 (5)	2.1 (4)	1.6 (4)	1.2 (4)	4.7
C_{b7}	3.2 (4)	2.9 (3)	3.9 (4)	0.8 (3)	0.9 (3)	1.1 (3)	3.3
C_{c1}	3.1 (3)	3.1 (3)	3.5 (4)	1.6 (3)	0.4 (3)	1.1 (3)	3.1
C_{c2}	8.2 (7)	6.7 (6)	4.0 (5)	5.3 (6)	0.3 (5)	0.6 (4)	5.0
C_{c3}	12.2 (11)	11.2 (10)	4.0 (5)	9.0 (9)	−0.8 (6)	−0.2 (6)	6.5
C_{c4}	13.8 (12)	10.4 (10)	3.6 (5)	8.2 (9)	−0.1 (6)	−0.1 (6)	7.0
C_{c5}	9.9 (9)	8.3 (8)	4.0 (5)	4.9 (7)	−1.2 (6)	0.8 (5)	6.4
C_{c6}	5.5 (5)	5.8 (6)	4.7 (6)	2.7 (4)	0.2 (4)	2.0 (4)	5.0
C_{c7}	3.4 (4)	3.1 (3)	3.8 (4)	1.3 (3)	0.4 (3)	1.7 (3)	3.2
O_3	5.9 (4)	5.7 (4)	5.4 (4)	0.6 (3)	0.1 (3)	3.2 (3)	5.4
W_2	6.1 (4)	7.8 (5)	5.2 (4)	3.6 (4)	1.4 (3)	2.0 (4)	5.9

[a] The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. The B_{ij}'s in Å² are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the ligand (a, b, or c), and a numerical subscript that follows the numbering scheme given in Figure 1 for the tropolonate ion. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table VI. Bond Distances and Polyhedral Edge Lengths in the Coordination Groups[a]

	Length, Å			Length, Å	
Type[b,c]	T_3SnCl	T_3SnOH	Type[b,c]	T_3SnCl	T_3SnOH
Sn–X	2.362 (4)	1.974 (6)	X–O_{c2}	3.115 (8)	2.914 (9)
Sn–O_{a1}	2.050 (6)	2.057 (5)			
			O_{a1}–O_{a2}[d]	2.593 (9)	2.600 (7)
Sn–O_{a2}	2.138 (6)	2.148 (5)	O_{a1}–O_{b1}	2.884 (9)	2.896 (8)
Sn–O_{b1}	2.130 (6)	2.139 (5)	O_{a1}–O_{b2}	3.017 (10)	3.055 (8)
Sn–O_{b2}	2.162 (7)	2.180 (6)	O_{a1}–O_{c1}	2.932 (10)	2.919 (8)
Sn–O_{c1}	2.128 (6)	2.133 (5)	O_{a1}–O_{c2}	3.031 (10)	3.020 (9)
Sn–O_{c2}	2.168 (7)	2.220 (7)			
			O_{a2}–O_{b2}	2.524 (10)	2.570 (9)
			O_{a2}–O_{c2}	2.517 (9)	2.611 (9)
X–O_{a2}	3.430 (8)	3.110 (8)	O_{b1}–O_{b2}[d]	2.554 (9)	2.537 (8)
X–O_{b1}	3.348 (8)	3.104 (9)	O_{b1}–O_{c1}	2.534 (9)	2.517 (8)
X–O_{b2}	3.121 (8)	2.852 (9)	O_{c1}–O_{c2}[d]	2.542 (9)	2.538 (8)
X–O_{c1}	3.296 (8)	3.056 (8)			

[a] Figures in parentheses are the estimated standard deviations. [b] Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the ligand (a, b, or c), and a numerical subscript that follows the numbering scheme given in Figure 1 for the tropolonate ion. [c] X represents the unique ligand, Cl in T_3SnCl or OH in T_3SnOH. [d] The bite of the ligand.

Sn–X bond, with the accompanying increase in nonbonding repulsive energy, is quite uncalled for. The positioning of the X ligand may, indeed, be partially responsible for the otherwise unexplained difference in the equatorial Sn–O_1 and Sn–O_2 bond lengths involving ligands b and c (Table VI); bonds of Sn–O_2 type are invariably longer by objectively significant amounts.

The molecular configuration observed for the T_3SnX molecules closely resembles that which would be obtained by substituting the monodentate X ligand for one of the bidentate tropolonato ligands in the theoretically expected (but as yet unproven) eight-coordinate tetrakis(tropolonato)tin(IV) stereoisomer of the dodecahedral *mmmm* type.[24] The observed coordination of the tropolonato ligands b and c is precisely that expected for the SnT_4 species, the cited rotation of the tropolonato ligand a from the ideal positioning in pentagonal-bipyramidal geometry takes it halfway to that demanded by dodecahedral geometry, and the rotation of the Sn–X bond puts it within 8 or 10° of the axis bisecting the fourth tropolonato ligand that is required to complete dodecahedral coordination in the SnT_4 molecule.

Table VII. Bond Angles Subtended at the Sn(IV) Atom in the Coordination Groups[a]

	Angle, deg			Angle, deg	
Type[b,c]	T_3SnCl	T_3SnOH	Type[b]	T_3SnCl	T_3SnOH
$XSnO_{a2}$	99.2 (2)	97.8 (2)	$O_{a1}SnO_{b2}$	91.5 (3)	92.3 (2)
$XSnO_{b1}$	96.3 (2)	97.9 (3)	$O_{a1}SnO_{c1}$	89.1 (3)	88.3 (2)
$XSnO_{b2}$	87.1 (2)	86.6 (3)	$O_{a1}SnO_{c2}$	91.8 (3)	89.7 (2)
$XSnO_{c1}$	94.3 (2)	96.1 (2)			
$XSnO_{c2}$	86.8 (2)	87.8 (3)	$O_{a2}SnO_{b2}$	71.9 (2)	72.9 (3)
			$O_{a2}SnO_{c2}$	71.5 (2)	73.4 (2)
$XSnO_{a1}$	175.7 (4)	174.0 (3)	$O_{b1}SnO_{c1}$	73.0 (3)	72.2 (2)
			$O_{b1}SnO_{b2}$	73.0 (2)	71.9 (2)
$O_{a1}SnO_{a2}$	76.5 (2)	76.2 (2)	$O_{c1}SnO_{c2}$	72.6 (2)	71.3 (2)
$O_{a1}SnO_{b1}$	87.2 (3)	87.3 (2)			

[a] Figures in parentheses are the estimated standard deviations. [b] Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the ligand (a, b, or c), and a numerical subscript that follows the numbering scheme given in Figure 1 for the tropolonate ion. [c] X represents the unique ligand, Cl in T_3SnCl or OH in T_3SnOH.

It is quite generally true that an appropriately chosen eight-coordination polyhedron requires only a modest increase in the nonbonding repulsive energy over that which characterizes any of the seven-coordination polyhedra, an observation that correlates with the more nearly uniform spatial distribution in the eight-coordinate case of the complexing bonds emanating from the central atom. For complexes that formally may be considered to be put together from closed-shell cations and anions, as in the present case, a marked preference on the part of the central atom for the best approximation in the given circumstances to a spatially uniform distribution of the bonding orbitals is anticipated. Consequently, the observed distortions of the T_3SnX configuration in the direction of apparent eight-coordination, particularly the rotation of the Sn–X bond, are the less surprising. It may then be emphasized that neither the monocapped trigonal prism nor the monocapped octahedron, both highly polar coordination polyhedra, bears any marked geometrical resemblance to either of the preferred eight-coordination polyhedra.[24] These considerations perhaps suggest why the T_3SnX species utilize a somewhat modified form of pentagonal-bipyramidal geometry.

It further appears that the *mmmm* dodecahedral stereoisomer of SnT_4, with an averaged Sn–O bond length of 2.16–2.17 Å, would have just two extremely short O···O inter-ring contacts of ~2.56 Å, as contrasted with three of these in the T_3SnX species, but it would have eight rather short O···O contacts of ~2.70 Å. The packing relations thus specified are a little tighter than those in the tetrakis(oxalato)-[36] and bis(nitrilotriacetato)zirconium(IV)[37] ions, are nearly as close-fitting as those involving C···C contacts between monodentate ligands in the octacyanomolybdate (IV) ion,[38] and are very much tighter than those which allow the tin tetranitrate molecule[39,40] to exist as a stable species in the absence of water.

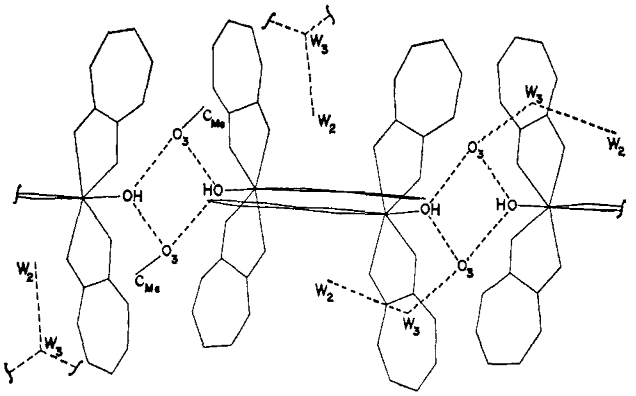

Figure 5. A drawing (adapted from a computer-drawn diagram of the partially disordered structure) illustrating the ordered arrangements of the solvate molecules corresponding to the compositions, $T_3SnOH \cdot H_2O \cdot CH_3OH$ (at left) and $T_3SnOH \cdot 3H_2O$ (at right); dashed lines are used for hydrogen bonds. The noncentrosymmetric hybrid of these patterns, occurring in its mutually antiparallel pair of orientations, is presumed to be the most prominent feature of the real arrangement of the solvate molecules in the $T_3SnOH \cdot (3 - 2x)H_2O \cdot xCH_3OH$ structure.

Bond lengths and angles within the tropolonato ligands are listed in Tables VIII and IX. The last two columns of each table give values averaged over the three tropolonato ligands of each molecule for bonds of similar chemical types; such averaging assigns effective C_2 symmetry to the principal axis of each ligand. The averaged C–C and C–O bond lengths from the T_3SnX molecules are utilized in the rather detailed discussion of tropolonato stereochemistry given in the accompanying paper.[3]

The structural roles played by the solvate molecules, H_2O and CH_3OH, in crystalline $T_3SnOH \cdot (3 - 2x)H_2O \cdot xCH_3OH$ can be elucidated by first noting that the Fouier peaks or atomic positions (Table III) labeled O_3 and W_2 correspond to oxygen atoms with normal thermal parameters (isotropic B values of 5.4 and 5.9 Å^2) whereas the xC_{Me} and $(1 - x)W_3$ peaks correspond roughly to half-atoms ($x \sim 1/2$) of carbon and oxygen with rather larger thermal parameters; the interatomic distances listed in Table X for the somewhat disordered arrangement of the solvate molecules then lend themselves to detailed analysis, as illustrated in Figure 5.

Joint consideration of the 1.46-Å O_3–C_{Me} and 1.27-Å W_3–C_{Me} distances (Table X) shows us that the former is interpretable as the O–C bond length in the methanol molecule provided W_3 is absent; if the fractional occupancy of the C_{Me} position is x, filling of the W_3 position may not exceed $1 - x$. The alternative interpretation of the apparent W_3–C_{Me} distance as the O–C bond length in methanol is precluded on two counts: the distance (1.27 Å) is unduly small and the O_3 peak corresponds to full occupancy. If, indeed, the O_3 peak be taken as the sum of xOH (from methanol) and $(1 - x)H_2O$, we are led to a solution of the substitutional disorder problem that, barring the precise value of x, is unique. The solvate molecules occur in two locally ordered patterns, each corresponding to a limiting value of x (0 or 1), that are used in approximately equal proportions and randomly distributed throughout the crystal. Figure 5 illustrates the disposition of the solvate molecules and the concomitant hydrogen bonding for each of the locally ordered patterns—or, otherwise put,

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(36) G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 250 (1963).

(37) J. L. Hoard, E. W. Silverton, and J. V. Silverton, *J. Amer. Chem. Soc.*, **90**, 2300 (1968).

(38) J. L. Hoard, T. A. Hamor, and M. D. Glick, *ibid.*, **90**, 3177 (1968).

(39) C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc. A*, 1949 (1967).

(40) The very small bite (2.14 Å) of the nitrate ion is responsible for the easy packing relations that allow stability of the anhydrous $Sn(NO_3)_4$ molecule in dodecahedral eight coordination.

Table VIII. Bond Lengths (Å) in the Tropolonato Ligands[a]

	Ligand a		Ligand b		Ligand c		Average[c]	
Type[b]	T_3SnCl	T_3SnOH	T_3SnCl	T_3SnOH	T_3SnCl	T_3SnOH	T_3SnCl	T_3SnOH
O_1–O_2[d]	2.593 (9)	2.600 (7)	2.554 (9)	2.537 (8)	2.542 (9)	2.538 (8)	2.548 (6)[e]	2.538 (1)[e]
O_1–C_1	1.300 (12)	1.321 (8)	1.284 (11)	1.287 (10)	1.285 (12)	1.289 (10)	1.287 (8)	1.285 (14)
O_2–C_7	1.269 (12)	1.270 (9)	1.286 (12)	1.273 (11)	1.297 (12)	1.269 (10)		
C_1–C_7	1.475 (13)	1.458 (10)	1.444 (13)	1.458 (11)	1.439 (15)	1.457 (11)	1.453 (15)	1.458 (0)
C_1–C_2	1.406 (15)	1.375 (11)	1.420 (14)	1.405 (13)	1.416 (14)	1.396 (12)	1.412 (8)	1.396 (12)
C_7–C_6	1.423 (14)	1.404 (10)	1.396 (14)	1.414 (13)	1.411 (15)	1.381 (14)		
C_2–C_3	1.398 (16)	1.382 (10)	1.410 (15)	1.365 (15)	1.392 (15)	1.378 (16)	1.392 (8)	1.377 (12)
C_6–C_5	1.388 (16)	1.396 (11)	1.384 (16)	1.389 (16)	1.381 (17)	1.350 (17)		
C_3–C_4	1.365 (21)	1.372 (9)	1.390 (17)	1.378 (16)	1.403 (20)	1.369 (18)	1.393 (12)	1.380 (7)
C_5–C_4	1.412 (21)	1.385 (13)	1.401 (18)	1.388 (17)	1.387 (20)	1.384 (19)		

[a] The figure in parentheses following each datum is the estimated standard deviation. [b] Atoms numbered to agree with Figure 1 and, for ligands b and c, to observe the quasi-mirror plane of the molecule. [c] The figure in parentheses following each averaged value is the mean deviation; the averaging assigns C_2 symmetry to each tropolonato ligand. [d] The bite of the ligand. [e] Average for ligands b and c; the bite of ligand a is distinctively larger (see text).

Table IX. Bond Angles (deg) in the Tropolonato Ligands[a]

	Ligand a		Ligand b		Ligand c		Average[c]	
Type[b]	T_3SnCl	T_3SnOH	T_3SnCl	T_3SnOH	T_3SnCl	T_3SnOH	T_3SnCl	T_3SnOH
O_1SnO_2	76.5 (3)	76.2 (2)	73.0 (3)	71.9 (2)	72.6 (3)	71.3 (2)	72.8 (2)[d]	71.6 (3)[d]
SnO_1C_1	116.9 (6)	117.0 (4)	117.9 (6)	119.4 (5)	118.1 (6)	119.5 (4)	117.7 (4)[d]	119.0 (5)[d]
SnO_2C_7	114.7 (6)	114.6 (4)	117.8 (6)	118.7 (5)	117.0 (5)	118.4 (5)		
$O_1C_1C_7$	115.4 (9)	115.0 (6)	116.7 (8)	115.2 (8)	116.1 (8)	116.2 (7)	115.6 (11)	115.3 (13)
$O_2C_7C_1$	116.1 (8)	117.0 (6)	114.6 (8)	114.7 (7)	114.6 (10)	113.8 (7)		
$C_1C_7C_6$	125.3 (9)	124.8 (7)	127.7 (9)	126.3 (8)	127.6 (10)	125.2 (8)	127.0 (12)	126.0 (16)
$C_7C_1C_2$	128.1 (9)	127.7 (6)	126.4 (9)	124.8 (8)	126.7 (10)	126.3 (8)		
$C_1C_2C_3$	129.3 (11)	130.4 (6)	129.0 (10)	131.0 (10)	129.1 (12)	130.0 (10)	129.4 (5)	130.9 (9)
$C_7C_6C_5$	129.4 (11)	130.8 (7)	130.4 (11)	130.4 (12)	129.5 (12)	132.6 (10)		
$C_2C_3C_4$	129.3 (12)	129.8 (6)	129.8 (10)	132.0 (11)	129.5 (11)	129.4 (11)	129.5 (2)	129.8 (4)
$C_6C_5C_4$	129.6 (12)	129.0 (7)	129.1 (10)	130.6 (10)	129.5 (12)	128.4 (11)		
$C_3C_4C_5$	128.6 (12)	127.4 (7)	127.4 (10)	124.8 (10)	127.7 (11)	127.9 (11)	127.9 (4)	126.7 (10)

[a] The figure in parentheses following each datum is the estimated standard deviation. [b] Atoms numbered to agree with Figure 1 and, for ligands b and c, to observe the quasi-mirror plane of the molecule. [c] The figure in parentheses following each averaged value is the mean deviation; the averaging assigns C_2 symmetry to each tropolonato ligand. [d] Average for ligands b and c.

Table X. Bond Parameters Involving the Solvate Molecules in $T_3SnOH \cdot (3 - 2x)H_2O \cdot xCH_3OH$

Bond type[a]	Length, Å	Angle type[a]	Angle, deg
OH–O_3	2.67	$O_3(OH)O_3'$	98
OH–O_3'	2.77	$(OH)O_3(OH)'$	82
O_3–W_3	2.67	$W_3W_2W_3'$	65
W_2–W_3	2.80	$W_2W_3W_2$	115
W_2–W_3'	2.96	$O_3W_3W_2$	119
O_3–C_{Me}[b]	1.46	$O_3W_3W_2'$	116
$W_3 \cdots C_{Me}$[c]	1.27	$W_3O_3(OH)$	105

[a] Notations (see also Figure 5): OH represents hydroxo of the T_3SnOH molecule; O_3 includes both xOH of methanol and $(1 - x)H_2O$; W_2 and W_3 are used for the other structural classes of water molecules; C_{Me} represents the methyl carbon of $x CH_3OH$; primed and unprimed pairings of symbols denote pairings of atoms related by a center of inversion. [b] Chemical bond in the methanol molecule. [c] Apparent separation, a statistical consequence of the substitutional disorder.

for the alternative crystalline arrangements corresponding to the limiting compositions, $T_3SnOH \cdot 3H_2O$ and $T_3SnOH \cdot H_2O \cdot CH_3OH$. The four-membered hydrogen-bonded grouping of $2O_3$ (as H_2O or methanolic OH) and 2OH from contiguous T_3SnOH molecules is characteristic of all compositions; one notes (Table X) that the bond angles are constrained to smaller than ideal values.

Although the geometry of the crystalline framework is well suited to the partial substitution of methanol for water molecules, it appears that, in otherwise thermodynamically favorable circumstances, the additional hydrogen bonding (O_3–W_3 and W_2—W_3) afforded by the ordered pattern corresponding to pure $T_3SnOH \cdot 3H_2O$ should lead to crystallization of the unsubstituted hydrate. Probably the dominant consideration favoring the mixed solvate as the product of recrystallization of hydrated T_3SnOH from methanol (see Experimental Section) is the fact that, in the solution, the chemical potential of the water is greatly depressed relative to that of the pure component, whereas the chemical potential of the methanol remains near that of the pure liquid. A complete ordering of the observed crystalline arrangement, most simply for an x of precisely $^1/_2$ to give a noncentrosymmetric sorting of the solvate molecules (W_2 excepted) in the otherwise centrosymmetric structure, must be accompanied by a decrease in entropy and, presumably, by a small decrease in energy; the entropic effects are expected to be, and apparently are, controlling to give the somewhat disordered phase.[41]

All that is significant in respect to the apparent C–H bond lengths in the T_3SnOH molecule, as calculated from the carbon and hydrogen positions (Tables III and IV), may be summarized as follows. The 15 distances average to 0.98 Å with 0.14 and 0.13 Å as the respective values of the mean deviation from the average and of the (root-mean-square) standard deviation for an individual datum.

(41) The ordered noncentrosymmetric arrangement of the solvate molecules would give the crystal a rather pronounced polarity. More than 10 years of experience in the use of a highly sensitive Geibe–Schiebe piezoelectric detector suggests that the absence of detectable piezoelectricity in crystals of the T_3SnOH solvate should be taken at face value.