Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

An Unusual Ternary Chloride of Tin and Tantalum, $Sn[Ta_2Cl_9]_2$

F. Albert Cotton,* Elizabeth Babaian-Kibala, Larry R. Falvello, and Maoyu Shang

Received November 7, 1989

One product of the reaction between $TaCl_5$ and tri-*n*-butyltin hydride is a green compound of formula $SnTa_4Cl_{18}$. The structure of this compound has several surprising features: (1) discrete face-sharing bioctahedral Ta_2Cl_9 units that show a distortion from D_{3h} symmetry; (2) Sn atoms in square antiprismatic coordination; (3) formation of crystals in the rare chiral space group $P6_122$ (or $P6_522$). From the structure and the fact that the compound is diamagnetic, its constituents are deduced to be Sn^{2+} and $[Ta_2Cl_9]^-$ ions. The distortion of the $[Ta_2Cl_9]^-$ ion is attributed to packing forces. The mean Sn–Cl distance is 2.918 [13] Å. The $[Ta_2Cl_9]^-$ ion has $Ta-Cl_t$ = 2.33 [2] Å (average), $Ta-Cl_b$ = 2.47 [1] Å (average), and Ta–Ta = 2.812 (3) Å. The unit cell has dimensions of a = 15.144 (4) Å, c = 26.930 (5) Å, V = 5348 (1) Å^3, and Z = 6.

Introduction

For some years in this laboratory, we have been investigating the non-organometallic chemistry of niobium and tantalum in their lower valence states, particularly II,[1] III,[2] and IV.[3] Entry into this chemistry has normally been by reduction of the pentahalides where the usual reducing agents have been Na/Hg or magnesium. More recently we have begun to explore other reducing agents, one of which is tri-*n*-butyltin hydride. We report here one example of its use where an entirely unexpected product, which incorporates the tin, was obtained. An additional feature of interest in this unexpected product, $SnTa_4Cl_{18}$, is that the tin atom, which we believe to be Sn^{II}, is coordinated in an unprecedented manner.

Experimental Section

All operations were conducted in an atmosphere of argon as the compound is extremely sensitive to both oxygen and water. $TaCl_5$ was purchased from Aesar Chemicals, and tri-*n*-butyltin hydride, Bu_3SnH, from Strem Chemicals. The magnetic susceptibility was measured on a Johnson Matthey magnetic susceptibility balance.

Preparation of $SnTa_4Cl_{18}$. To a slurry of $TaCl_5$ (3.0 g, 8.37 mmol) in 50 mL of toluene, cooled to −78 °C, was added, dropwise, Bu_3SnH (2.25 mL, 8.37 mmol). During the addition, a very slight color change was observed. After several hours of stirring at −78 °C, the cooling bath was removed, the mixture was allowed to come to room temperature, and stirring was continued for 15 h. At this time, the flask contained a green-brown precipitate and dark green supernatant liquid. The precipitate, which was produced with a final yield of 0.55 g, partially dissolved in THF, forming trinuclear $Ta_3Cl_9(THF)_4$. This compound, accompanied with other related structures, will be discussed in future publications. The solution was, on the other hand, filtered through 2.0 cm of Celite into a Schlenk tube and layered with 20 mL of hexane. As interdiffusion proceeded, a green, microcrystalline product was deposited on the walls of the tube. Yield: 0.32 g; 11%.

Often a light brown powder, as yet uncharacterized, coprecipitated with the product. We have not found any solvent for the green product with which it does not react, and thus it can be freed from the brown solid only by physical separation. The crystals used for structure determination were obtained from a reaction carried out in benzene rather than toluene. In addition, we kept the reaction vessel as still as possible while the crystals formed.

Table I. Crystal Data for $Sn[Ta_2Cl_9]_2 \cdot C_6H_6$

compound	$Sn[Ta_2Cl_9]_2 \cdot C_6H_6$
formula	$Ta_4Cl_{18}SnC_6H_6$
fw	1558.77
space group	$P6_522$
a, Å	15.144 (4)
b, Å	15.144 (4)
c, Å	26.930 (5)
α, deg	90.0
β, deg	90.0
γ, deg	120.0
V, Å^3	5348.4
Z	6
d_{calc}, g/cm^3	2.904
μ(Mo Kα), cm^{-1}	141.516
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
temp, °C	−80
transm factors: max, min	0.9961, 0.6519
R^a	0.04711
$R_w{}^b$	0.06064

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Atomic Positional and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $Sn[Ta_2Cl_9]_2 \cdot C_6H_6$

atom	x/a	y/b	z/c	B_{eqv},^{a} Å^2
Ta(1)	0.4716 (2)	1.1884 (2)	0.65690 (8)	2.60 (5)
Ta(2)	0.3628 (2)	0.9959 (2)	0.61146 (8)	2.26 (4)
Sn	0.301	0.6987 (2)	0.583	2.20 (8)
Cl(1)	0.5033 (8)	1.0425 (8)	0.6734 (5)	2.4 (3)
Cl(2)	0.2665 (9)	0.8338 (8)	0.6495 (4)	2.8 (3)
Cl(3)	0.4279 (9)	0.9146 (9)	0.5583 (5)	3.1 (4)
Cl(4)	0.298 (1)	1.0523 (9)	0.6809 (5)	3.7 (4)
Cl(5)	0.245 (1)	1.002 (1)	0.5621 (6)	5.6 (5)
Cl(6)	0.4996 (9)	1.1464 (9)	0.5725 (5)	3.3 (4)
Cl(7)	0.411 (1)	1.287 (1)	0.6278 (7)	7.0 (5)
Cl(8)	0.648 (1)	1.3063 (9)	0.6522 (4)	3.5 (4)
Cl(9)	0.492 (1)	1.228 (1)	0.7416 (5)	4.6 (5)
C(1)	0.347 (8)	0.214 (7)	0.964 (3)	16 (4)*
C(2)	0.386 (7)	0.150 (7)	0.957 (3)	14 (4)*
C(3)	0.364 (8)	0.291 (7)	0.908 (4)	17 (4)*

^{a}Starred values denote atoms that were refined isotropically. The equivalent isotropic displacement parameter, B_{eqv}, is calculated as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22}$ (cos $c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12}\ 2ac \times (\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

X-ray Crystallography. A crystal was mounted in an inert atmosphere on the tip of a quartz fiber with epoxy glue and transferred in dry nitrogen to a CAD-4 diffractometer where it was protected by a constant stream of cold nitrogen (ca. −80 °C). All intensity data were corrected for polarization and Lorentz effects. Empirical absorption corrections were applied based upon ψ-scans of six reflections at χ near 90°. Photographs showed hexagonal (trigonal) symmetry of the lattice. A summary of information pertinent to the characterization of the crystal, collection of intensity data, and the refinement of the structure will be found in Table I.

The positions of the Ta atoms and several of the Cl atoms were determined from a Patterson map (SHELXS-86). A series of alternating refinements and difference Fourier maps allowed the location of the remaining Cl atoms and the Sn atom, as well as the atoms of an interstitial benzene molecule.

The systematic absences, combined with our photographic determination that the Laue group is $6/mmm$, show unambiguously that the

---

(1) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5506.

(2) (a) Cotton, F. A.; Diebold, M. P.; Feng, X.; Roth, W. J. *Inorg. Chem.* **1988**, *27*, 3413. (b) Cotton, F. A.; Shang, M. *J. Am. Chem. Soc.* **1988**, *110*, 7719. (c) Canich, J. A. M.; Cotton, F. A.; Duraj, S. A.; Falvello, L. R. *Inorg. Chim. Acta* **1988**, *143*, 185.

(3) (a) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1988**, *27*, 3596. (b) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1988**, *27*, 2347.

0020-1669/90/1329-2591$02.50/0

Table III. Selected Bond Distances (Å) and Angles (deg) for $Sn[Ta_2Cl_9]_2{\cdot}C_6H_6$[a]

Bond Distances			
Ta(1)–Ta(2)	2.812 (3)	Ta(2)–Cl(5)	2.26 (2)
Ta(1)–Cl(1)	2.523 (14)	Ta(2)–Cl(6)	2.422 (10)
Ta(1)–Cl(4)	2.479 (11)	Sn–Cl(2)	2.952 (13)
Ta(1)–Cl(6)	2.453 (13)	Sn–Cl(2)′	2.952 (13)
Ta(1)–Cl(7)	2.25 (2)	Sn–Cl(3)	2.924 (12)
Ta(1)–Cl(8)	2.355 (12)	Sn–Cl(3)′	2.924 (11)
Ta(1)–Cl(9)	2.339 (14)	Sn–Cl(8)	2.893 (11)
Ta(2)–Cl(1)	2.511 (13)	Sn–Cl(8)′	2.893 (11)
Ta(2)–Cl(2)	2.370 (10)	Sn–Cl(9)	2.902 (13)
Ta(2)–Cl(3)	2.40 (2)	Sn–Cl(9)′	2.902 (12)
Ta(2)–Cl(4)	2.452 (15)		

Bond Angles			
Cl(1)–Ta(1)–Cl(4)	79.2 (5)	Cl(2)–Sn–Cl(3)′	77.7 (3)
Cl(1)–Ta(1)–Cl(6)	78.6 (5)	Cl(2)–Sn–Cl(8)	150.3 (3)
Cl(1)–Ta(1)–Cl(7)	164.0 (5)	Cl(2)–Sn–Cl(8)′	75.8 (4)
Cl(1)–Ta(1)–Cl(8)	92.0 (5)	Cl(2)–Sn–Cl(9)	142.1 (4)
Cl(1)–Ta(1)–Cl(9)	89.9 (6)	Cl(2)–Sn–Cl(9)′	111.4 (4)
Cl(4)–Ta(1)–Cl(6)	105.9 (4)	Cl(2)′–Sn–Cl(3)′	77.7 (3)
Cl(4)–Ta(1)–Cl(7)	91.6 (5)	Cl(2)′–Sn–Cl(3)	66.9 (3)
Cl(4)–Ta(1)–Cl(8)	166.1 (5)	Cl(2)′–Sn–Cl(8)	75.8 (4)
Cl(4)–Ta(1)–Cl(9)	84.6 (4)	Cl(2)′–Sn–Cl(8)′	150.3 (3)
Cl(6)–Ta(1)–Cl(7)	91.7 (6)	Cl(2)′–Sn–Cl(9)	111.4 (4)
Cl(6)–Ta(1)–Cl(8)	82.5 (4)	Cl(2)′–Sn–Cl(9)′	142.1 (4)
Cl(6)–Ta(1)–Cl(9)	162.4 (6)	Cl(3)–Sn–Cl(3)′	132.7 (4)
Cl(7)–Ta(1)–Cl(8)	99.3 (5)	Cl(3)–Sn–Cl(8)	89.0 (4)
Cl(7)–Ta(1)–Cl(9)	102.3 (7)	Cl(3)–Sn–Cl(8)′	110.4 (4)
Cl(8)–Ta(1)–Cl(9)	84.6 (4)	Cl(3)–Sn–Cl(9)	148.8 (5)
Cl(1)–Ta(2)–Cl(2)	90.0 (4)	Cl(3)–Sn–Cl(9)′	76.0 (5)
Cl(1)–Ta(2)–Cl(3)	91.8 (5)	Cl(3)–Sn–Cl(8)	110.4 (4)
Cl(1)–Ta(2)–Cl(4)	79.9 (5)	Cl(3)′–Sn–Cl(8)′	89.0 (4)
Cl(1)–Ta(2)–Cl(5)	162.4 (6)	Cl(3)′–Sn–Cl(9)	76.0 (5)
Cl(1)–Ta(2)–Cl(6)	79.4 (4)	Cl(3)′–Sn–Cl(9)′	148.8 (5)
Cl(2)–Ta(2)–Cl(4)	83.4 (4)	Cl(8)–Sn–Cl(8)′	131.2 (3)
Cl(2)–Ta(2)–Cl(5)	102.0 (5)	Cl(8)–Sn–Cl(9)	66.1 (4)
Cl(2)–Ta(2)–Cl(6)	162.8 (6)	Cl(8)–Sn–Cl(9)′	77.0 (4)
Cl(3)–Ta(2)–Cl(4)	166.3 (5)	Cl(8)′–Sn–Cl(9)	77.0 (4)
Cl(3)–Ta(2)–Cl(5)	101.8 (6)	Cl(8)′–Sn–Cl(9)′	66.1 (4)
Cl(3)–Ta(2)–Cl(6)	81.2 (5)	Cl(9)–Sn–Cl(9)′	80.3 (6)
Cl(4)–Ta(2)–Cl(5)	88.6 (6)	Ta(1)–Cl(1)–Ta(2)	67.9 (4)
Cl(4)–Ta(2)–Cl(6)	107.7 (4)	Ta(1)–Cl(4)–Ta(2)	69.5 (4)
Cl(5)–Ta(2)–Cl(6)	91.5 (5)	Ta(1)–Cl(6)–Ta(2)	70.4 (3)
Cl(2)–Sn–Cl(2)′	81.9 (4)	Cl(2)–Ta(2)–Cl(3)	85.6 (4)
Cl(2)–Sn–Cl(3)	66.9 (4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

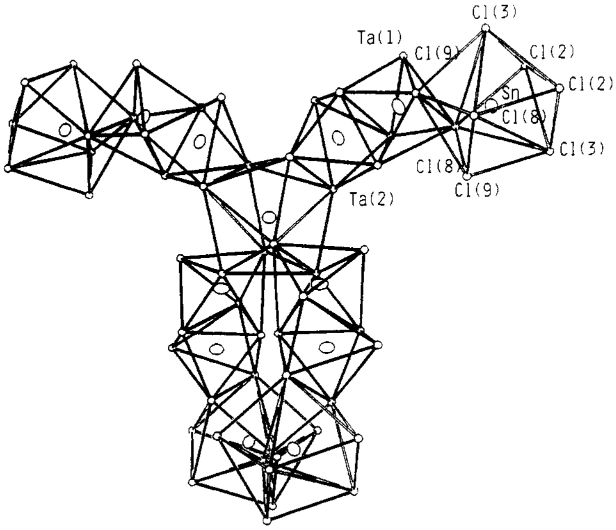

Figure 1. Partial view of the packing of the Ta_2Cl_9 units, showing how they create one of the approximately square antiprismatic cavities (six per unit cell) in which the tin atoms reside.

space group must be $P6_122$ or its enantiomorph $P6_522$. The structure was refined to convergence in both, and for the particular crystal used $P6_522$ was found to give significantly lower R values (Hamilton T test) and a better quality of fit. The positional parameters and equivalent isotropic displacement parameters are listed in Table II.

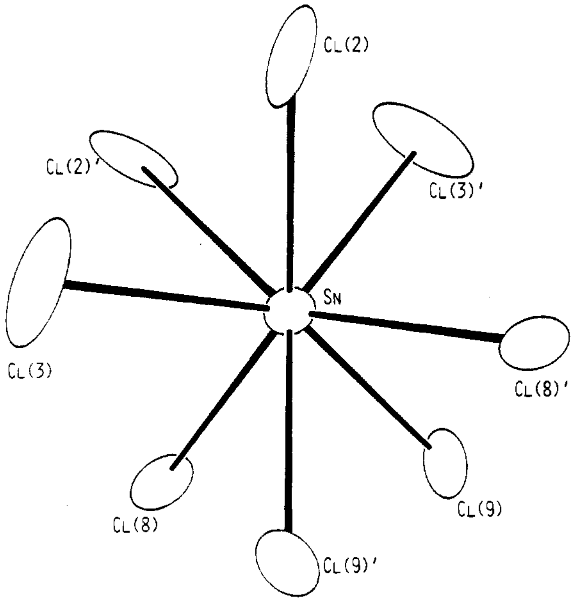

Figure 2. View of one tin atom and its eight nearest neighbors, viewed down what would be the $\bar{8}$ axis of an ideal square antiprism.

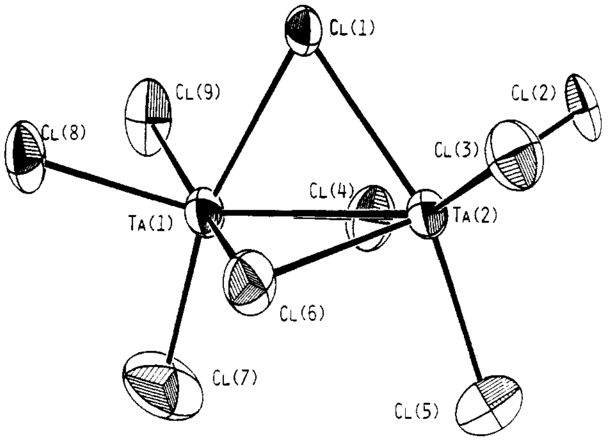

Figure 3. ORTEP[10] drawing of the Ta_2Cl_9 unit, showing the atom numbering scheme. Each atom is represented by its ellipsoid of thermal displacement drawn at the 40% probability level.

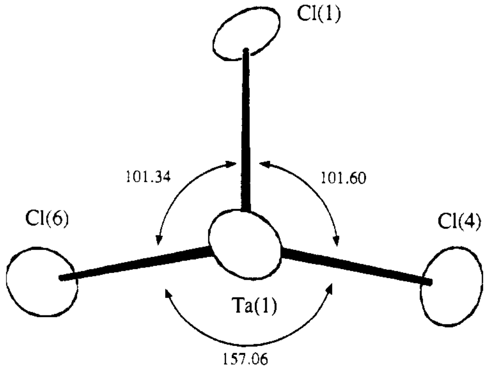

Figure 4. View of the central part of the Ta_2Cl_9 unit with the Ta–Ta axis perpendicular to the plane of the drawing. The three angles are dihedral angles between Ta(2)–Cl(n)–Ta(1) planes.

Results and Discussion

The formation of the product described here, which incorporates a tin ion surrounded by chlorine atoms of the $[Ta_2Cl_9]^-$ ion, was certainly not anticipated. However, this product is more interesting than any we had envisioned. Its principal dimensions are presented in Table III, and important aspects of its structure are shown in

Figure 1–4. Given the composition, $Sn[Ta_2Cl_9]_2 \cdot C_6H_6$, and the fact that it is diamagnetic, we conclude that it contains Sn^{2+} and $[Ta_2Cl_9]^-$ ions with Ta–Ta single bonds.

The Ta–Ta distance of 2.812 (3) Å is consistent with the existence of such a bond and the angles in the central portion provide some further support. The three Ta(1)–Cl_b–Ta(2) angles are in the range 67.9–70.4°, all smaller than expected in the absence of an attractive interaction between the metal atoms. However, because of the distortion of the Ta_2Cl_9 unit from D_{3h} symmetry, the usual arguments[4] concerning the M–Cl_b–M and Cl_b–M–Cl_b angles cannot be applied in the normal way. This distortion, and possible reasons for it, will be discussed later.

The crystal structure is unusual in several respects. The adoption of a very uncommon, inherently chiral space group by a substance consisting of simple, nonchiral components is odd to begin with. The packing of the $[Ta_2Cl_9]^-$ ions is such that they spiral around the 6_5 axes. This creates a series of interstices, each on a 2 axis, with a shape closely approximating a square antiprism. The tin ions reside in the centers of these interstices, on the 2 axes. This stacking is depicted in Figure 1, and the coordination sphere of the tin ion, viewed down the approximate $\bar{8}$ (S_8) axis, is shown in Figure 2.

It is clear from Figure 2 that the square antiprism is imperfect, but this description is the best of the simple polyhderal designations that one might propose. The two parallel square faces of the ideal square antiprism are defined by Cl(2), Cl(3), Cl(9)′, and Cl(8)′ for the upper one and Cl(8), Cl(9), Cl(3)′, and Cl(2)′ for the lower one, as seen in Figure 2. These two sets of atoms are indeed confined to each of two planes that are parallel to within very small deviations. In addition, the Sn–Cl distances, which have a mean value of 2.918 [9] Å, lie within the range 2.893 (11)–2.952 (13) Å. The difference between the two extreme values is barely if at all significant, being just above the 3σ level, and none of the individual values differs from the mean by an amount that is significant at the 3σ level.

The nature of the coordination sphere of the tin ion, as just described, constitutes strong support for its assignment as a tin(II) ion rather than tin(IV). According to Shannon and Prewitt radii,[5] Sn–Cl distances of eight-coordinate tin would be 3.03 and 2.62 Å for Sn^{2+} and Sn^{4+}, respectively. Clearly, the observed distance, 2.92 Å, is much more consistent with the Sn^{2+} value. It must be admitted however, that the estimates of the eight-coordinate radii for tin are both very uncertain. We can find no data for Sn^{2+} in the literature; the value given by Shannon and Prewitt is derived from unpublished data. For Sn^{4+} the only case of eight-coordination seems to be provided by $Sn(NO_3)_4$, which has dodecahedral coordination,[6] and the high coordination number for such a small ion may only be possible because the coordinated atoms are rather small and are furthermore held together in close pairings within the nitrate ions. Thus, the qualitative fact that the tin atom is coordinated by eight chlorine atoms may, in itself, be taken as a strong indication that it must be Sn^{II} and not Sn^{IV}. The nearly regular shape of the coordination polyhedron about the Sn^{2+} ion shows that there is no stereochemically active lone pair. This, together with the rather long Sn–Cl distances and high coordination number lead to the conclusion that the tin–chlorine interactions are of a highly electrostatic nature. In contrast, when Sn^{II} is coordinated by six chlorine atoms, there usually is a stereochemically active lone pair and the "octahedron" is severely distorted so that there are three short bonds[7,8] (ca. 2.5 Å) and three very long ones (ca. 3.5 Å).

The remaining structural aspect of this unusual compound that must be examined in detail is the distortion of the $[Ta_2Cl_9]^-$ ion from the ideal (D_{3h}) face-sharing bioctahedral structure that might have been anticipated for it. An overall view of the ion is shown in Figure 3, while Figure 4 focuses on the most conspicuous aspect of the distortion, namely, the marked deviation of the set of bridging Cl atoms from 3-fold symmetry. We believe that this distortion is primarily an indirect result of the packing of the Ta_2Cl_9 units about the tin atoms. We note in Table III that all four of the angles Cl(2)–Ta(2)–Cl(5), Cl(3)–Ta(2)–Cl(5), Cl(8)–Ta(1)–Cl(7), and Cl(9)–Ta(1)–Cl(7) are around 100° whereas other acute Cl–Ta–Cl angles are in the range 78–92°. This can be attributed to packing forces pushing Cl(5) and Cl(7) toward the central plane defined by the three bridging atoms. This, in turn pushes Cl(4) and Cl(6) up toward Cl(1).

The possibility that there might be a hydrogen atom also bridging the Ta atoms, lying between Cl(4) and Cl(6) and opposite to Cl(1), was carefully considered and rejected for the following reasons. First, this would require that the tin atom be tin(IV) in order to continue to be consistent with the diamagnetism of the compound, and we have already explained why the assignment of tin(II) is greatly preferred. Second, the insertion of a hydrogen atom into the plane of the bridging atoms does not actually make sense sterically. We have carried out calculations of H···Cl contacts for an H atom placed along the extension of a line running from Cl(1) through the center of the Ta–Ta bond. The range of these positions was limited by Ta–H distances of 1.7–1.9 Å. Throughout this range, the H···Cl contacts to Cl(4), Cl(5), Cl(6), and Cl(7) were far too close to be credible, namely, 2.6–2.8 Å. Third, a very careful examination of electron density difference maps in this region revealed no evidence of any extra density. Fourth, according to the work of Sattelberger et al.[9] on tantalum compounds with μ-H atoms, Ta–H stretching bands occur in the infrared at around 1280 cm^{-1}, but a search of this region revealed nothing.

It should be emphasized that this compound is extremely sensitive to air and moisture and does not dissolve in most common solvents except for those with which it appears to react. Thus, many techniques that might help to substantiate the composition of the $[Ta_2Cl_9]^-$ and Sn^{2+} ions are not employable. With special effort Mössbauer or ESCA spectroscopies might have been applied, but it is not at all certain that they could unequivocally distinguish between tin(II) and tin(IV) in view of the unprecedented environment of the tin atom. The very considerable time and effort required to obtain such results was not, therefore, considered to be justified.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant No. A-494. We also thank Dr. P. A. Kibala for his assistance in calculating the position of the possible hydrogen atom and Dr. R. L. Luck for his assistance in the examination of the electron density difference maps.

Supplementary Material Available: Tables of complete, crystal data, complete bond distances and angles, posititional and isotropic displacement factors, and general displacement parameters for $Sn[Ta_2Cl_9]_2 \cdot C_6H_6$ (7 pages); a table of calculated and observed structure factors for $Sn[Ta_2Cl_9]_2 \cdot C_6H_6$ (6 pages). Ordering information is given on any current masthead page.

---

(4) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

(5) (a) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925. (b) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

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

(7) Poulsen, F. R.; Rasmussen, S. E. *Acta Chem. Scand.* **1970**, *24*, 150.

(8) Zuckerman, J. J.; Ng, S. W. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 297.

(9) Leutkens, M. L.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1983**, *105*, 4474.

(10) Johnson, C. K. ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.