*Inorganica Chimica Acta*, 75 (1983) 265–270

# The Crystal and Molecular Structure of Di-Ammonium Trichlorostannate(II) Chloride Monohydrate.
## Structural Correlations for Chlorotin(II) Derivatives

PHILIP G. HARRISON*, BERNARD J. HAYLETT and TREVOR J. KING†

*Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, U.K.*

Received March 25, 1983

*Crystals of the title compound are orthorhombic, space group $Pna2_1$, with a = 12.331(3), b = 8.379(2), c = 9.293(3) Å. The structure was solved by usual Patterson and Fourier techniques to a final R-value of 0.04 for 1278 independent, non-zero reflections. The tin forms three short (2.563(1), 2.561(5), 2.551(6) Å) bonds to three adjacent chlorine atoms, with a fourth contact to the chloride ion at 3.222(2) Å. Neighbouring [$SnCl_3\cdots Cl^-$] units are connected by two longer Sn···Cl bridges at 3.386(6) and 3.376(5) Å forming a chain structure, and completing a severely distorted octahedral environment at tin. The anionic chains, ammonium cations and the water molecule participate in a three-dimensional network of hydrogen bonds. The relationship of this structure to those of related compounds is discussed.*

## Introduction

The structure and spectroscopy of the trihalogenostannate(II) ions ($SnX_3^-$, X = F, Cl, Br, I) in solution and the solid state have aroused continued interest since Volkringer, Tchakirian and Freymann [1, 2] proposed the existence of $SnCl_3^-$ and $SnBr_3^-$ in acid solutions of the tin(II) halide. Subsequently, Kamenar and Grdenic [3] showed that the double salt $KCl\cdot KSnCl_3\cdot H_2O$ contained discrete pyramidal [$SnCl_3^-$] anions, although no addition contacts to the tin atom were considered. The possible formation of the [$SnCl_4^{2-}$] was first proposed by Prytz [4], and also later on the basis of infrared and Mössbauer data for $BaSnCl_4$ by Goldstein and Tiwan [5], but has only been unequivocally characterised in the complex $[Co(NH_3)_6][SnCl_4]Cl$ by Huber and his coworkers [6] who also examined the related $[Co(en)_3][SnCl_3]Cl_2$ complex [7]. The [$SnCl_3^-$] anion in the latter complex has similar structural parameters to other complexes containing this species, with all other Sn···Cl contacts being >4 Å, whereas the latter has a distorted pseudo-trigonal bipyramidal $SnCl_4^{2-}$ anion with the tin lone-pair occupying an equatorial position ($Sn–Cl_{ax}$, 3.003(2), 2.669(2) Å, $Sn–Cl_{eq}$, 2.526(2), 2.467(2) Å; $Cl_{ax}–Sn–Cl_{ax}$, 164.69(6)°; $Cl_{eq}–Sn–Cl_{eq}$, 89.98(5)°).

Described in this paper are the synthesis, crystal structure and spectroscopic properties of diammonium trichlorostannate(II) chloride monohydrate, which appears to possess an anionic component intermediate between $SnCl_3^-$ and $SnCl_4^{2-}$.

## Experimental

### *Synthesis*

Tin(II) chloride dihydrate (25 g) was dissolved in concentrated hydrochloric acid (20 $cm^3$) and water (10 $cm^3$) to give a clear solution with pH *ca.* 0. A solution of concentrated ammonia (d = 0.880) and water (1:1 v/v) was added with stirring until the pH of the mixture was *ca.* 1. 2 *M* ammonia solution was then slowly added until a permanent precipitate was formed. This was cleared by boiling the solution and further quantities of hot 2 *M* ammonia were added until a slight precipitate appeared. The solution was then filtered rapidly through a hot filter tube into a warm flask and allowed to cool slowly.

The product was deposited rapidly over a small temperature range and comprised colourless needle crystals. These were filtered off, washed with ice cold water, dry methanol and dry ether, and dried by suction overnight. (Found: H 3.37, N 8.86, Cl 44.95, Sn 37.5%; Calculated for $(NH_4)_2\cdot SnCl_3\cdot Cl\cdot H_2O$: H 3.20, N 8.90, Cl 45.08, Sn 37.73%).

### *Structure Determination and Refinement*

#### *Crystal data*

$H_{10}Cl_4N_2OSn$; M = 314.59; Orthorhombic; space group $Pna2_1$; *a* = 12.331(3), *b* = 8.379(2), *c* =

---

*Author to whom correspondence should be addressed.

†Deceased.

0020-1693/83/$3.00

TABLE I. Final Fractional Atomic Coordinates for $(NH_2)_2 \cdot SnCl_3 \cdot Cl \cdot H_2O$ (estimated standard deviations in parentheses).

| *Atom* | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Sn(1) | –0.01200(3) | –0.01022(4) | 0.2500* |
| Cl(1) | 0.1817(1) | 0.1009(2) | 0.2462(8) |
| Cl(2) | –0.0616(4) | 0.1967(7) | 0.0581(6) |
| Cl(3) | –0.0596(4) | 0.1959(8) | 0.4419(6) |
| Cl⁻(1) | –0.2730(1) | –0.1087(2) | 0.2491(9) |
| O(1) | –0.0322(6) | –0.4168(7) | 0.257(2) |
| N(1) | –0.186(1) | –0.362(2) | 0.476(2) |
| N(2) | –0.172(1) | –0.378(2) | 0.014(2) |

*The z coordinate of the tin atom was fixed at 0.2500.

9.293(3) Å; $U = 960.17$ Å$^3$; $D_m$(flotation) = 2.02 g cm$^{-3}$; $D_c = 2.18$ g cm$^{-3}$; $Z = 4$; $F(000) = 590$; Mo-$K_\alpha$ ($\lambda$ = 0.71069 Å); (Mo-$K_\alpha$) = 34.41 cm$^{-1}$. Crystal dimensions = 0.2 × 0.3 × 0.3 mm$^3$.

Intensity data were collected over a $\theta$ range of 0 to 30.0° corresponding to the range: $0 \leqslant h \leqslant 20$; $0 \leqslant k \leqslant 16$; $0 \leqslant l \leqslant 16$.

1278 independent, non-zero reflections for which $I > 3\sigma(I)$ were corrected for Lorentz and polarisation effects, but not for absorption ($\mu = 34.41$ cm$^{-1}$). Atomic positions of non-hydrogen atoms were located by usual Patterson and Fourier techniques. All atomic coordinates were refined by full-matrix anisotropic least-squares methods, converging to a convenient R-value of 0.0466.

At this stage an agreement analysis of $F_c$ on $F_o$ was computed and a Chebyschev [8] weighting scheme was applied to the observed intensities:

$$W = \frac{1}{[A_oT'_o(X) + A_1T'_1(X) + \ldots A_3T'_3(X)]}$$

where $(X) = f_o/f_o(\max)$, $\{f_o(\max) = 321.26\}$, and $A_n$ values were calculated from a least-squares minimisation of $\Sigma[(F_o - F_c)^4]$ giving $A_o = 271.50$, $A_1 = 397.54$, $A_2 = 149.45$ and $A_3 = 16.164$.

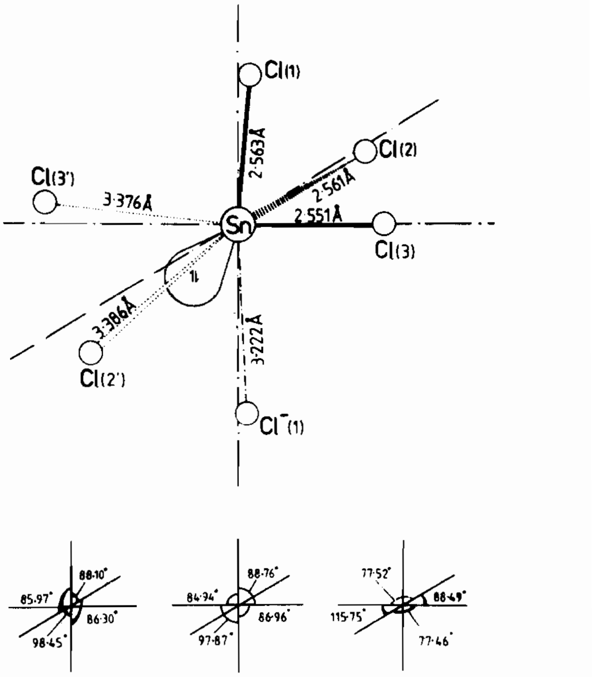

Fig. 1. Diagrammatic view of the first coordination sphere of tin in $(NH_4)_2 \cdot SnCl_3 \cdot Cl \cdot H_2O$ showing bond distance and angle data.

Further full-matrix least-squares refinement reduced the R-value to 0.0421.

Atomic scattering factors used were those for the neutral atom except in the case of Cl⁻(1) where the value for the singly charged anion was used. All computations were performed using the CRYSTALS suite of programs [9].

Final fractional atomic coordinates and anisotropic temperature factors are listed in Tables I and II respectively. A list of interatomic contacts and angles are given in Table III.

TABLE II. Final Anisotropic Thermal Parameters for $(NH_4)_2 \cdot SnCl_3 \cdot Cl \cdot H_2O$ (estimated standard deviations in parentheses).[a]

| *Atom* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Sn(1) | 3.29(2) | 3.45(2) | 2.91(2) | 0.14(8) | 0.65(5) | –0.39(1) |
| Cl(1) | 2.57(5) | 4.37(7) | 3.35(8) | –0.1(3) | 0.0(2) | –0.06(5) |
| Cl(2) | 3.5(2) | 3.6(2) | 3.8(2) | –0.6(2) | –1.1(2) | –0.1(2) |
| Cl(3) | 3.2(2) | 6.0(3) | 2.7(2) | 0.4(2) | –0.3(1) | –0.1(2) |
| Cl⁻(1) | 4.67(8) | 4.05(7) | 3.19(7) | –0.3(3) | 0.3(3) | 0.66(6) |
| C(1) | 5.4(3) | 4.5(2) | 5.8(6) | 0.5(6) | 2.8(6) | 0.2(2) |
| N(1) | 2.5(5) | 4.9(8) | 3.6(6) | –0.5(5) | 0.1(4) | 0.2(4) |
| N(2) | 2.9(5) | 3.8(5) | 3.2(5) | 0.6(5) | –1.1(4) | 0.0(4) |

[a] $U_{ij}$ are of the form: $10^2 \cdot \exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2klU_{23}b^*c^* + 2hlU_{13}a^*c^*)]$.

TABLE III. Interatomic Contacts (A) and Angles (°) in $(NH_4)_2 \cdot SnCl_3 \cdot Cl \cdot H_2O$ (estimated standard deviations in parentheses).

(a) *Contact Distances*

| | | | |
|---|---|---|---|
| Sn(1)–Cl(1) | 2.563(1) | O(1)···N(1) | 2.90(2) |
| Sn(1)–Cl(2) | 2.561(5) | O(1)···N(2) | 2.91(2) |
| Sn(1)–Cl(3) | 2.551(6) | N(1)···Cl(2′) | 3.44(2) |
| Sn(1)–Cl$^-$(1) | 3.322(2) | N(1)···Cl$^-$(1) | 3.17(1) |
| Sn(1)–Cl(2′) | 3.386(6) | N(1)···Cl(2″) | 3.24(2)* |
| Sn(1)–Cl(3′) | 3.376(5) | N(2)···Cl(3′) | 3.44(2) |
| Sn(1)···O(1) | 3.793(6) | N(2)···Cl$^-$(1) | 3.23(2) |
| O(1)···Cl$^-$(1) | 3.263(7) | N(2)···Cl(3″) | 3.30(2)* |

*Hydrogen-bonding between adjacent chains.

(b) *Angles*

| | | | |
|---|---|---|---|
| Cl(1)–Sn(1)–Cl(2) | 88.1(2) | Sn(1)···O(1)···Cl$^-$(1) | 75.6(1) |
| Cl(1)–Sn(1)–Cl(3) | 88.8(2) | Sn(1)···O(1)···N(1) | 108.0(5) |
| Cl(1)–Sn(1)–Cl(2′) | 86.0(2) | Sn(1)···O(1)···N(2) | 108.0(4) |
| Cl(1)–Sn(1)–Cl(3′) | 84.9(2) | N(1)···O(1)···N(2) | 80.2(2) |
| Cl(1)–Sn(1)–Cl$^-$(1) | 173.0(1) | | |
| Cl(2)–Sn(1)–Cl(3) | 88.5(1) | O(1)···N(1)···Cl(2′) | 72.2(4) |
| Cl(2)–Sn(1)–Cl(2′) | 164.8(1) | O(1)···N(1)···Cl$^-$(1) | 86.9(5) |
| Cl(2)–Sn(1)–Cl(3′) | 77.5(1) | O(1)···N(1)···Cl(2″) | 146.6(6) |
| Cl(2)–Sn(1)–Cl$^-$(1) | 86.3(2) | Cl$^-$(1)···N(1)···Cl(2″) | 74.5(4) |
| Cl(3)–Sn(1)–Cl(2′) | 77.5(1) | | |
| Cl(3)–Sn(1)–Cl(3′) | 164.8(1) | O(1)···N(2)···Cl(3′) | 139.5(6) |
| Cl(3)–Sn(1)–Cl$^-$(1) | 87.0(2) | | |
| Cl(2′)–Sn(1)–Cl(3′) | 115.1(1) | O(1)···N(2)···Cl$^-$(1) | 125.0(6) |
| Cl(2′)–Sn(1)–Cl$^-$(1) | 98.5(2) | O(1)···N(2)···Cl(3″) | 56.7(3) |
| Cl(3′)–Sn(1)–Cl$^-$(1) | 97.9(2) | Cl$^-$(1)···N(2)···Cl(3″) | 107.8(5) |

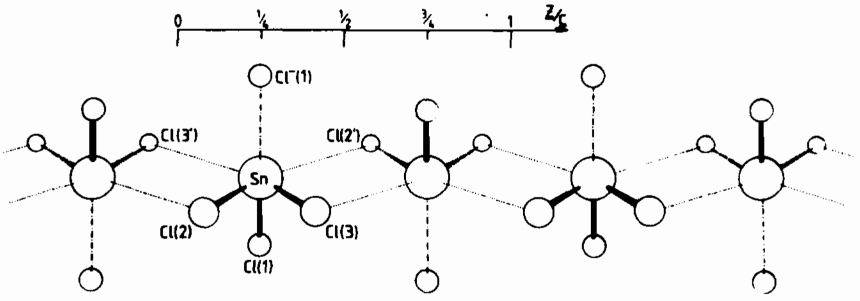

Fig. 2. Diagrammatic view of the linear polymer anion of $(NH_4)_2 \cdot SnCl_3 \cdot Cl \cdot H_2O$.

## Discussion

### *The Structure of $(NH_4)_2 \cdot SnCl_3 \cdot Cl \cdot H_2O$*

A diagrammatic representation of the coordination sphere of the tin atom is depicted in Fig. 1. The tin atom is surrounded in a distorted octahedral fashion by five chlorine atoms and a chloride ion. The three bonds to the chlorine atoms in the $SnCl_3^-$ moiety are typical of that structure, as are the intervening angles. A comparison of these data with those for some similar substances is given in Table IV.

The bond to the chloride ion is longer (3.222(2) Å) and is directed almost 180° away from Cl(1) (173.03(5)°). Diametrically opposite Cl(2) and Cl(3), and at increased distances (3.386(6) and 3.376(5) Å respectively), are their counterparts, each in a different, adjacent $SnCl_3^-$ moiety. Thus, the whole anionic structure is a linear polymer of edge-sharing octahedra, bridged by Cl(2) and Cl(3) atoms. Cl(1) and $Cl^-$ protrude at right-angles with each alternately above and below the polymer plane (Fig. 2). The octahedral formation is distorted, with all the bonds bent away from the apex of the SnCl(1)Cl(2)Cl(3)

TABLE IV. Comparison of the Structural Parameters of Some $SnCl_3^-$ Containing Species.

| | $(NH_4)_2 \cdot SnCl_3Cl \cdot H_2O$[a] | $KCl \cdot KSnCl_3 \cdot H_2O$[b] | $Sr(SnCl_3)_2 \cdot 5H_2O$[c] | $CsSnCl_3$[d] |
|---|---|---|---|---|
| Sn–Cl(1) | 2.563(1) Å | 2.54 Å | 2.608(4) Å | 2.52(1) Å |
| Sn–Cl(2) | 2.561(5) Å | 2.54 Å | 2.577(5) Å | 2.50(1) Å |
| Sn–Cl(3) | 2.551(6) Å | 2.63 Å | 2.627(4) Å | 2.55(1) Å |
| Cl(1)–Sn–Cl(2) | 88.10(17)° | 90.8° | 93.86(13)° | 86.9(2)° |
| Cl(2)–Sn–Cl(3) | 88.49(05)° | 87.7° | 87.06(13)° | 92.3(3)° |
| Cl(3)–Sn–Cl(1) | 88.76(18)° | 87.7° | 86.16(12)° | 90.2(3)° |

[a] This work. [b] Ref. 3. [c] Ref. 12. [d] Ref. 13.

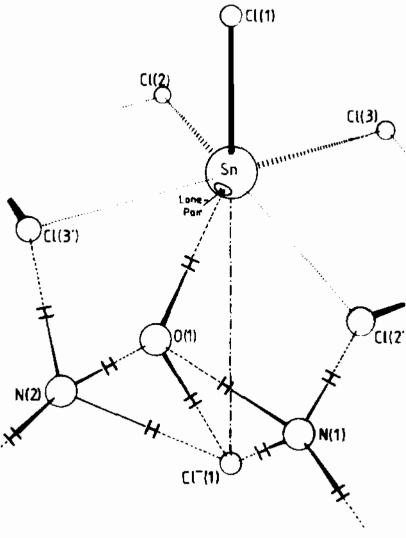

Fig. 3. Diagrammatic view of the asymmetric unit of $(NH_4)_2 \cdot SnCl_3 \cdot Cl \cdot H_2O$.

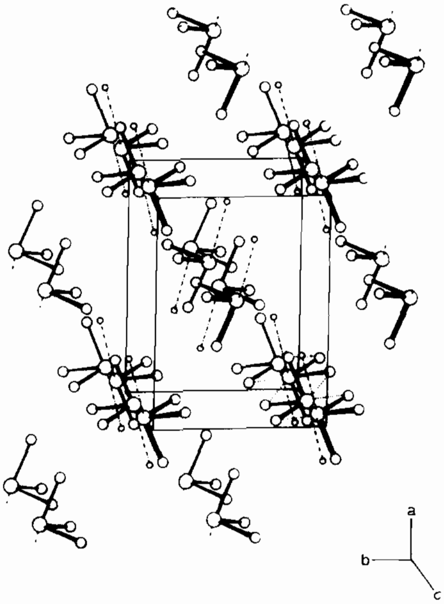

Fig. 4. Perspective view of the unit cell of $(NH_4)_2 \cdot SnCl_3 \cdot Cl \cdot H_2O$ (showing anionic components only for clarity).

pyramid (Fig. 1), presumably to accommodate the tin lone-pair which is weakly stereochemically active in this species. The oxygen atom of the water molecule is to be found 3.793(6) Å from the tin in the direction of the supposed lone-pair and symmetrically placed above the enlarged Cl(2)′Cl(3)′Cl⁻ face of the octahedron. The two nitrogen atoms, N(1) and N(2), are to be found 4.208(18) and 4.263(17) Å from the tin atom, forming pyramidal arrangements with Cl⁻OCl(2)′ and Cl⁻OCl(3)′ respectively. The nitrogen–oxygen distances (2.901(24), 2.911(24) Å) are indicative of hydrogen-bonding, and the O–Cl′ distances (3.422(14), 3.362(14) Å), although quite large, are comparable with those, presumed, bifurcated hydrogen bonds in $K_2SnCl_4 \cdot H_2O$ [10] (3.32(9), 3.42(9), 3.42(9), 3.52(9), 3.56(9), 3.56(9) Å). The upper limit for O–H···Cl bonding has been postulated as 3.78 Å by Falk and Knop [11]. A diagrammatic representation of the whole asymmetric unit is given in Fig. 3. The chains are hydrogen-bonded together by N–H···Cl″ interactions (*in Table III).

A perspective view of the unit cell is shown in Fig. 4; the bridging links are shown for one chain only.

### *Structural Correlations for Chlorotin(II) Derivatives*

Table V compares the tin-119 Mössbauer data for $(NH_4)_2SnCl_3 \cdot Cl \cdot H_2O$ with those for related chlorotin(II) systems. (Note that compounds *f* and *i*, despite having an identical composition, are clearly structurally different as indicated by their distinctly different Mössbauer parameters. The structural data for the compound studied here (compound *i*) show the two $[NH_4]$ cations to be chemically equivalent). From the data, it would appear that, for this group of related compound, the steady decrease of isomer shift is parallelled by an increase in quadru-

TABLE V. Comparison of the Tin-119 Mössbauer Data for Chlorotin(II) Systems.

| | *Compound* | *I.S.*[a] | *Q.S.*[a] |
|---|---|---|---|
| *a* | $Ba(SnCl_3)_2$[b] | 4.23 | 0.72 |
| *b* | $SnCl_2$[c] | 4.099 | 0.606 |
| *c* | $BaSnCl_4$[b] | 3.97 | 0.70 |
| *d* | $SnCl_2 \cdot SC(NH_2)_2$[c] | 3.711 | 0.981 |
| *e* | $CsSnCl_3$[d] | 3.69 | 0.90 |
| *f* | $NH_4Cl \cdot NH_4SnCl_3 \cdot H_2O$[d] | 3.69 | 0.95 |
| *g* | $NH_4SnCl_3$[d] | 3.61 | 0.91 |
| *h* | $SnCl_2 \cdot 2H_2O$[c] | 3.587 | 1.186 |
| *i* | $(NH_4)_2SnCl_3 \cdot Cl \cdot H_2O$[c] | 3.576 | 1.069 |
| *j* | $Me_4NSnCl_3$[e] | 3.51 | 1.08 |
| *k* | $Et_4NSnCl_3$[f] | 3.47 | 1.00 |
| *l* | $Bu_4NSnCl_3$[g] | 3.12 | 1.37 |

[a] $mm\ s^{-1}$. [b] Ref. 5. [c] This work. [d] Ref. 14. [e] Ref. 15. [f] Ref. 16. [g] Ref. 17.

pole splitting. This empirical relationship* may be rationalised by a consideration of the structural modifications taking place down the group. The principal types of environments for the tin atom in these compounds are illustrated in Fig. 5. The environment adopted by a particular compound will be dependent in part on crystal packing considerations, and, for the trichlorostannate(II) derivatives, partly on the extent to which the cationic charge is shielded from the anion.

The derivatives exhibiting the highest isomer shifts with the lowest quadrupole splittings are tin(II) chloride and the two barium chlorostannates(II), $BaSnCl_4$ and $Ba(SnCl_3)_2$.

Now, tin(II) chloride has the $PbCl_2$ lattice structure, and the barium compounds $Ba(SnCl_3)_2$ and $BaSnCl_4$ can be regarded as $SnCl_2$ with 1/3 and 1/2 of the tin atoms replaced by barium, respectively. Hence the structure and thus the electronic configuration around the tin atoms remains similar for all three compounds. The tin valence electrons are confined mainly to $p^3$ hybridised orbitals, allowing the lone-pair to reside in the spherical 5s orbital (Fig. 5(a)), giving a high electron density at the nucleus and an almost cubic symmetry of the electron density resulting in high isomer shift and low quadrupole splitting, respectively.

Towards the bottom of Table V, the cation becomes increasingly shielded and increasingly bulky, preventing the anions from forming the polymeric

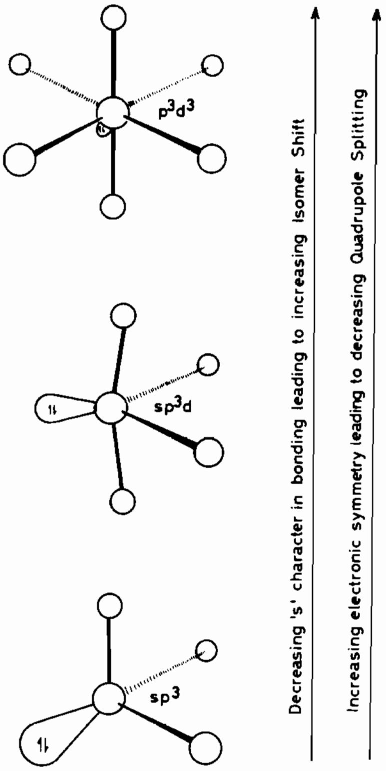

Fig. 5. Coordination types of chlorotin(II) derivatives.

chains. The conformation of lowest energy for the now separated $SnCl_3^-$ ions is a pseudo-tetrahedral form. The valence electrons of the tin atom now occupy $sp^3$ orbitals with, consequently, a directional lone-pair (Fig. 5(c)), which causes severe distortion of the tetrahedral arrangement into a pyramidal form with the angles at tin *ca.* 90°. Thus, in these cases, the s electron density at the tin nucleus is small and the cubic symmetry of the electron cloud is lost, resulting in a lower isomer shift and a higher quadrupole splitting, respectively, than the two barium derivatives and tin(II) chloride. No Mössbauer data are available for the tetrachlorostannate(II) derivative $[Co(NH_3)_6][SnCl_4]Cl$, which possesses the structure illustrated in Fig. 5(b), and hence should exhibit intermediate values for the isomer shift and quadrupole splitting. The presently studied compound (compound *f*) has a structure which is intermediate between those in Figs. 5(b) and 5(c), with three short (2.551(6), 2.561(5) and 2.563(1) Å) and one longer (3.222(2) Å) tin–chlorine bonds, and hence has intermediate isomer shift and quadrupole splitting values.

The two compounds *d* and *h* ($SnCl_2 \cdot S{:}C(NH_2)_2$ and $SnCl_2 \cdot 2H_2O$) have higher and lower isomer shift, respectively, than would be expected from the above reasoning (*vice versa* for q.s.). This is because, in both cases, one of the chlorine atoms of the

---

*There is, of course, no theoretical basis for such a relationship.

coordination sphere has been replaced by another atom. In the first case, compound *d*, by sulphur which has a lower electronegativity than chlorine, and in the second case, compound *h*, by oxygen, which has a higher electronegativity than chlorine. This results in the compounds experiencing higher and lower isomer shift values, respectively.

## References

1 H. Volkringer, A. Tchakirian and M. Freymann, *C.R.*, *199*, 292 (1934).
2 A. Tchakirian and H. Volkringer, *C.R. 2CO*, 1758 (1935).
3 B. Kamenar and D. Grdenic, *J. Inorg. Nucl. Chem.*, *24*, 1039 (1962).
4 M. Prytz, *Z. Anorg. Chem.*, *172*, 147 (1928).
5 M. Goldstein and P. Tiwari, *J. Inorg. Nucl. Chem.*, *37*, 1550 (1975).
6 H. J. Haupt, F. Huber and H. Preut, *Z. Anorg. Allg. Chem.*, *422*, 97 (1976).
7 H. J. Haupt, F. Huber and H. Preut, *Z. Anorg. Allg. Chem.*, *422*, 255 (1976).
8 'Computing Methods in Crystallography', Ed. J. S. Rollet, p. 40, Pergamon, Oxford (1965).
9 J. R. Carruthers' 'CRYSTALS' program, Oxford University, Crystallography Computer Programs.
10 M. Falk, C.-H. Huang and O. Knop, *Can. J. Chem.*, *52*, 2380 (1974).
11 M. Falk and D. Knop, 'Water – A Comprehensive Treatise', Vol. 2, Ed. F. Frantz, Plenum Press; New York (1973), Chapter 2.
12 H. J. Haupt, F. Huber and H. W. Sandbote, *Z. Anorg. Allg. Chem.*, *435*, 191 (1977).
13 F. R. Poulsen and S. E. Rasmussen, *Acta Chem. Scand.*, *24*, 150 (1970).
14 S. R. A. Bird, J. D. Donaldson and J. Silver, *J. Chem. Soc., Dalton*, 1950 (1972).
15 V. I. Baronovskii, V. P. Sargeev and B. E. Dzevitskii; *Doklady Phys. Chem.*, *184*, 55 (1969).
16 R. J. H. Clark, L. Maresca and P. J. Smith, *J. Chem. Soc. (A)*, 2687 (1970).
17 M. Goldstein and G. C. Tok, *J. Chem. Soc. (A)*, 2303 (1971).