# *X*-Ray Crystal Structure of the Complex of 15-Crown-5 (1,4,7,10,13-Pentaoxacyclopentadecane) with Diaquatetrachlorotin(IV) at 120 K *

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The crystal structure of the complex formed between $SnCl_4(H_2O)_2$ and 15-crown-5 has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 15.985(3)$, $b = 12.512(4)$, $c = 9.869(1)$ Å, and $\beta = 107.37(1)°$. The structure, which was refined to $R = 0.0441$ for 3 771 observed reflections, consists of octahedral $SnCl_4(H_2O)_2$ units linked by bifurcated hydrogen bonds from the water molecules to the 15-crown-5 molecules to form polymeric arrays. The water molecules are *trans* to each other. This, the first report of a *trans* arrangement (the *cis* configuration being that found hitherto), is relevant to the interpretation of Mössbauer data.

Macrocyclic polyethers are known to form second-sphere complexes with some metal compounds.[1] In the case of tin compounds the complexing properties of crown ethers depend on the valence state of the metal. With tin(II) acceptors the metal is bound directly to the oxygen atoms of the crown,[2,3] whereas the crown ether in the presence of water acts as a second-sphere ligand with tin(IV) compounds instead of complexing the metal directly[4] (see below).

In the course of determining the crystal structures of a number of products formed by treating tin(II) acceptors with crown ethers in oxygen and oxygen-free atmospheres, we identified the oxidised product from the tin(II) chloride–15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane, L) system as having an identical chemical composition to the tin(IV) adduct $SnCl_4 \cdot 2H_2O \cdot L$ reported by Cusack *et al.*[4] We report here the crystal structure of $SnCl_4(H_2O)_2L$, the results of which are relevant to the interpretation of the Mössbauer spectroscopic parameters.

## Experimental

*Preparation.*—The compound $SnCl_4(H_2O)_2L$ was prepared by the aerial oxidation of hydrated tin(II) chloride and 15-crown-5 in methanol. 15-Crown-5 (1.0 g) was added to tin(II) chloride dihydrate (2.06 g) in methanol (5 cm³). Diffraction-quality crystals were grown over 6 d. The presence of tin(IV) was confirmed by reaction with hydrogen sulphide and is consistent with the following element analyses [Found: C, 22.7; H, 4.7; Cl, 26.9; Sn (atomic absorption), 23.0. Calc. for $C_{10}H_{24}Cl_4O_7Sn$: C, 23.2; H, 4.7; Cl, 27.4; Sn, 23.0%]. The molecular formula, which was unequivocally confirmed by the successful solution of the crystal structure, is identical to that reported by Cusack *et al.*[4] for the product of reaction between tin(IV) chloride and 15-crown-5 in methanol.

*Crystallography.*—*Crystal data.* $C_{10}H_{24}Cl_4O_7Sn$, $M = 516.7$, monoclinic, $a = 15.985(3)$, $b = 12.512(4)$, $c = 9.869(1)$ Å, $\beta = 107.37(1)°$, $U = 1\,884.0$ Å³, $F(000) = 1\,272$, $D_m = 1.74$ g cm$^{-3}$ (flotation), $Z = 4$, $D_c = 1.84$ g cm$^{-3}$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu = 24.3$ cm$^{-1}$. Absences consistent with space group $P2_1/n$.

*Intensity data collection and structure refinement.* A crystal with approximate dimensions 0.10 × 0.22 × 0.42 mm was mounted in a general orientation on a Nonius CAD4 automatic four-circle diffractometer and intensity data collected at 120 K in the $\omega$—$2\theta$ scan mode out to $\theta = 30°$ using monochromatised Mo-$K_\alpha$ radiation. Cell dimensions were determined from the refined setting angles of 25 reflections located by a search routine. The space group was determined from the systematic absences. Data were transferred to a VAX 11/750 computer, Lorentz and polarisation corrections applied, systematic absences rejected, and equivalent reflections merged. The crystal was stable under data collection. Of the 5 000 reflections measured, 3 771 were classified as observed, *i.e.* $I_{net} > 3.0\sigma(I)$. Scattering factors and dispersion corrections were taken from ref. 5. Calculations were carried out by using the CRYSTALS Issue 8 package[6] and plots were drawn by the program ORTEP.[7] The structure was solved by Patterson and Fourier methods and successfully refined by full-matrix least squares in space group $P2_1/n$ to an $R$ factor of 0.0441 ($R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$ 0.0443) with unit weights and anisotropic thermal factors for the non-hydrogen atoms. The data were corrected for absorption. Hydrogen atoms were placed in calculated positions and given a common refined thermal parameter. The atomic positions are listed in Table 1, interatomic distances and valence angles in Table 2 and torsion angles in Table 3.

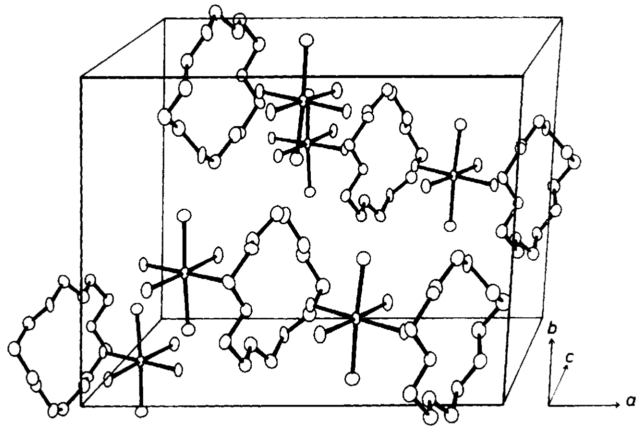

**Figure 1.** Crystal structure of $SnCl_4(H_2O)_2L$

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* *Supplementary data available* (No. SUP 56585, 4 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

**Table 1.** Atomic co-ordinates ( × $10^5$ for Sn, × $10^4$ for other atoms) with estimated standard deviations in parentheses

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| Sn | 12 840(3) | 24 179(3) | 38 229(4) | C(12) | 6 100(5) | 10 023(5) | 4 018(8) |
| Cl(2) | 1 757(1) | 2 361(1) | 1 749(1) | O(13) | 6 577(3) | 9 309(4) | 3 391(5) |
| Cl(3) | 1 257(1) | 517(1) | 3 884(2) | C(14) | 6 363(5) | 9 432(5) | 1 899(7) |
| Cl(4) | 1 410(1) | 4 301(1) | 3 871(2) | C(15) | 6 785(5) | 8 530(5) | 1 337(8) |
| Cl(5) | 725(1) | 2 473(1) | 5 815(1) | O(16) | 6 403(3) | 7 564(3) | 1 630(4) |
| C(6) | 6 075(5) | 5 699(6) | 5 506(1) | C(17) | 6 849(5) | 6 619(5) | 1 418(8) |
| O(7) | 5 398(3) | 6 494(4) | 5 083(5) | C(18) | 6 456(5) | 5 705(5) | 2 019(7) |
| C(8) | 5 258(5) | 7 102(6) | 6 242(7) | O(19) | 6 573(3) | 5 948(4) | 3 476(5) |
| C(9) | 5 828(5) | 8 084(6) | 6 570(7) | C(20) | 6 178(5) | 5 195(5) | 4 178(8) |
| O(10) | 5 639(3) | 8 696(4) | 5 325(5) | O(21) | 2 596(3) | 2 368(4) | 5 178(4) |
| C(11) | 6 147(5) | 9 623(6) | 5 470(8) | O(22) | −10(3) | 2 485(3) | 2 454(4) |

**Table 2.** Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Tin co-ordination

| | | | |
|---|---|---|---|
| Sn-O(22) | 2.107(4) | Cl(3)-Sn-Cl(4) | 176.04(7) |
| Sn-O(21) | 2.125(4) | Cl(2)-Sn-O(22) | 87.3(1) |
| Sn-Cl(4) | 2.364(2) | Cl(2)-Sn-O(21) | 91.9(1) |
| Sn-Cl(3) | 2.379(1) | Cl(2)-Sn-Cl(4) | 90.01(6) |
| Sn-Cl(2) | 2.386(2) | Cl(2)-Sn-Cl(3) | 90.26(7) |
| Sn-Cl(5) | 2.391(2) | Cl(5)-Sn-O(22) | 89.4(1) |
| | | Cl(5)-Sn-O(21) | 91.4(1) |
| O(21)-Sn-O(22) | 179.0(2) | Cl(5)-Sn-Cl(4) | 90.32(6) |
| Cl(4)-Sn-O(22) | 92.0(1) | Cl(5)-Sn-Cl(3) | 89.64(6) |
| Cl(4)-Sn-O(21) | 87.4(1) | Cl(5)-Sn-Cl(2) | 176.71(6) |
| Cl(3)-Sn-O(22) | 92.0(1) | | |
| Cl(3)-Sn-O(21) | 88.7(1) | | |

(*b*) 15-Crown-5 group

| | | | |
|---|---|---|---|
| C(6)-O(7) | 1.437(9) | C(20)-C(6)-O(7) | 107.8(5) |
| C(6)-C(20) | 1.51(1) | C(8)-O(7)-C(6) | 114.5(2) |
| O(7)-C(8) | 1.445(8) | C(9)-C(8)-O(7) | 112.0(6) |
| C(8)-C(9) | 1.51(1) | C(8)-C(9)-O(10) | 107.3(5) |
| C(9)-O(10) | 1.402(8) | C(9)-O(10)-C(11) | 113.3(5) |
| O(10)-C(11) | 1.399(9) | C(12)-C(11)-O(10) | 108.5(6) |
| C(11)-C(12) | 1.50(1) | C(11)-C(12)-O(13) | 108.9(6) |
| C(12)-O(13) | 1.430(9) | C(12)-O(13)-C(14) | 112.8(5) |
| O(13)-C(14) | 1.417(8) | C(15)-C(14)-O(13) | 107.8(6) |
| C(14)-C(15) | 1.50(1) | C(14)-C(15)-O(16) | 107.2(6) |
| C(15)-O(16) | 1.422(8) | C(17)-O(16)-C(15) | 114.2(5) |
| O(16)-C(17) | 1.428(8) | C(18)-C(17)-O(16) | 106.6(6) |
| C(17)-C(18) | 1.51(1) | C(17)-C(18)-O(19) | 106.9(5) |
| C(18)-O(19) | 1.427(8) | C(18)-O(19)-C(20) | 113.9(5) |
| O(19)-C(20) | 1.424(8) | C(6)-C(20)-O(19) | 109.0(5) |

**Table 3.** Torsion angles (°)

| | |
|---|---|
| C(6)-O(7)-C(8)-C(9) | 89.5(5) |
| O(7)-C(8)-C(9)-O(10) | 57.5(5) |
| C(8)-C(9)-O(10)-C(11) | −178.0(5) |
| C(9)-O(10)-C(11)-C(12) | 162.6(5) |
| O(10)-C(11)-C(12)-O(13) | −70.7(5) |
| C(11)-C(12)-O(13)-C(14) | 162.5(5) |
| C(12)-O(13)-C(14)-C(15) | −170.6(5) |
| O(13)-C(14)-C(15)-O(16) | 63.2(5) |
| C(14)-C(15)-O(16)-C(17) | −168.3(5) |
| C(15)-O(16)-C(17)-C(18) | 170.2(5) |
| O(16)-C(17)-C(18)-O(19) | −57.9(5) |
| C(17)-C(18)-O(19)-C(20) | 175.6(5) |
| C(18)-O(19)-C(20)-C(6) | −161.2(5) |
| O(19)-C(20)-C(6)-O(7) | 70.9(5) |
| C(20)-C(6)-O(7)-C(8) | −176.2(5) |

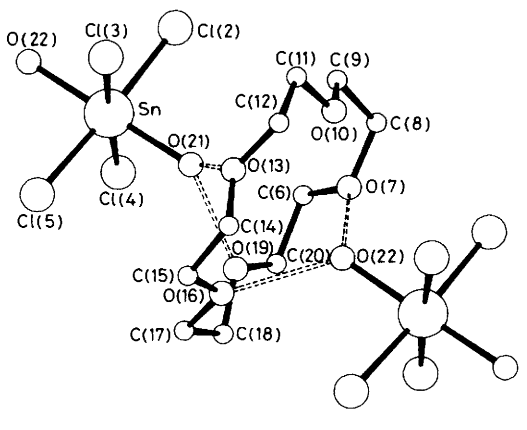

**Figure 2.** Part of the polymeric array. Atom numbering is in accordance with Table 1

## Results and Discussion

The crystal structure, part of which is shown in Figure 1, is polymeric, being composed of $SnCl_4(H_2O)_2$ units which are connected to crown ether molecules by hydrogen bonding. The interesting feature of the structure as compared with other hydrated tin(IV) chloride complexes is the *trans* positioning of the water molecules (see below) (Figure 2). The two water oxygen atoms in the $SnCl_4O_2$ unit are bifurcated, 2.657(6) Å from the nearest two oxygens of the crown. Each crown ether is thus shared by two $SnCl_4(H_2O)_2$ units, four of the five ether oxygens taking part in the hydrogen bonding. Figure 3 shows details of the crown ether conformation.

All previous examples of the unit $SnCl_4(H_2O)_2$ adopt the *cis* configuration.[8] Cusack *et al.*[4] suggested that the Mössbauer spectrum of the present complex indicates the *trans*-$SnX_4L_2$ arrangement, where L may be *either* (*a*) an oxygen atom of a crown ether or (*b*) a water molecule, which may be involved in hydrogen bonding with the crown ether. The latter is the case for the corresponding *cis* 18-crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane) complex. Therefore, our results show that the *trans*-oxygen interpretation is correct, that the oxygens belong to the water molecules, and that the crown is present as a second-sphere ligand. Although all previously known structures adopt the *cis* arrangement it would be speculative at this stage to assume that this necessarily relates to the lower-energy arrangement. The energy associated with the $SnCl_4(H_2O)_2$ fragment is only one of a sum of components defining the overall energy. Clearly, the structural changes which result on replacing 18-crown-6 by 15-crown-5 illustrate that the conformational preferences of the macrocycles, considered in the context of the hydrogen bonding, decisively influence the arrangements of the ligands about tin. Another example of a second-sphere cyclic ether complex is *cis*-diaquatetrabromo(1,4-dioxane)-tin(IV)[9] in which two dioxane molecules are hydrogen bonded

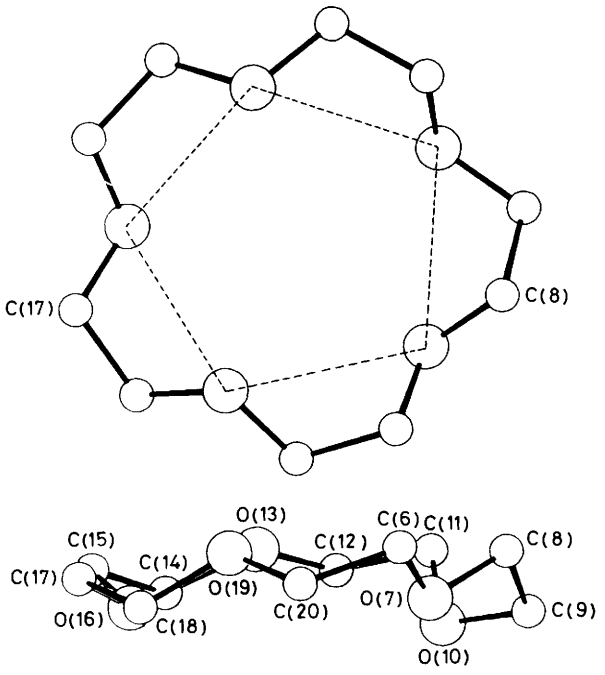

**Figure 3.** Top: the crown ether (non-hydrogen atoms) viewed in the direction normal to the mean $O_5$ plane. Bottom: view along a direction in the mean $O_5$ plane

to one *cis*-$SnBr_4(H_2O)_2$ unit. For the present structure the values of the C–O–C–C and O–C–C–O torsion angles indicate little strain in the adopted conformation.

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