

Complexes of Some Crown Ethers with Tin(II) in Methanol Solution. Synchrotron X-Ray Absorption Studies on the 12-Crown-4 and 15-Crown-5 Complexes

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The changing coordinations about the metal atom on adding 12-crown-4 (12CR4) and 15-crown-5 (15CR5) to solutions of tin(II) chloride in methanol have been explored by means of EXAFS. Instead of assuming bond lengths from supposedly appropriate models and fixing them in order to extract coordinations about tin, constraints that relate given bond lengths to their respective coordination numbers were developed using the Brown and Shannon relationship.

The considerable increases in the total coordination numbers found for tin(II) in the solutions containing the crowns are consistent with strong coordination between these ligands and tin. It is evident that there is equilibrium between several species in each solution, and the average coordination numbers suggest that the main species in the 12CR4 and 15CR5 solutions are $[\text{SnCl}_2 \cdot 12\text{CR4} \cdot \text{MeOH}]$ and $[\text{SnCl} \cdot 15\text{CR5} \cdot 2\text{MeOH}]^+$, respectively. The results are also consistent with the $[\text{Sn}(15\text{CR5})_2]^{2+}$ cation being a component in the latter system.

The unusual complexing properties of macrocyclic polyethers towards a wide range of acceptors are well established.¹ Although relatively little studied, the information that is available on the complexes formed with *p*-block elements shows that these interesting donor properties extend also to them. A prominent structural feature of complexes, and other materials, containing *p*-group elements in their lower valence states is the part played by their lone pairs in producing irregular coordinations. To some extent it would appear that this otherwise general feature may be departed from by some macrocyclic crown ether adducts.² Thus, although all crystallographic studies on tin(II) complexes with neutral donor molecules hitherto have revealed that the environments of tin(II) atoms are consistent with the lone pair being stereochemically active, the ¹¹⁹Sn Mössbauer spectroscopic results of Herber and Carrasquillo³ on a number of solid tin(II) complexes with the macrocyclic polyether 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) are consistent with the ligand complexing tin in a manner which renders the lone pair stereochemically inactive. In the absence of the crystal structures this conclusion is, of course, not unequivocal.

To date, there have been but a few structural studies on tin(II) complexes in solution. Concentrated aqueous solutions of tin(II) perchlorate have been studied by X-ray diffraction but it was not possible to reveal the complete

hydration structure of the tin(II) environment because of overlapping peaks in the overall radial distribution curve.⁴ More recently, EXAFS (extended X-ray absorption fine structure) studies on aqueous solutions of tin(II) perchlorate have shown a hydration structure about tin(II) in which the tin lone pairs are stereochemically active.⁵

The purpose of the present study is to exploit the unique advantage of EXAFS in probing the geometric environment of a specific element; in this case, to examine how the coordination about tin(II) changes as crown ethers of increasing coordinating capability are added to solutions of tin(II) chloride in methanol.

Experimental

EXAFS transmission measurements at room temperature were carried out at the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory, England, at the tin *K*-edge (0.42 Å, 29.5 KeV). The short-wavelength X-rays were produced by the 5 T wiggler magnet and the facilities of station 9.2. Data were reduced to χ -curves by means of the EXCALIB and EXBACK programs from the SRS program library, and transferred with appropriate partial-wave phase shifts δ_1 to UMIST for structure refinement.

All solutions were in methanol with the following compositions: $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2.0 g) in methanol (8.8 cm³); $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2.0 g) and 12-crown-4 (1.0 g) in methanol (8.0 cm³); $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2.05 g) and 15-crown-5 in methanol (8.0 cm³).

Theory and method

Owing to the similarity in the lengths of Sn(II)–O and Sn(II)–Cl bonds, which lie within the range (2.2–2.8 Å), values derived by EXAFS studies when these bonds are simultaneously present are liable to considerable correlation. Preliminary EXAFS least-squares refinements for the present solutions soon revealed that the values obtained by independently refining the two bond lengths are unreliable, as indicated by the large estimated standard deviations (e.s.d.). This unreliability is further compounded when attempts are made to extract the coordination numbers. Rather than fixing the bond lengths (by assuming values from supposedly appropriate model compounds) and investigating the coordination about the tin atom, we opted to develop constraints which relate both types of bond length to their respective coordination numbers.

These constraints were derived from the bond-length versus bond-strength relationships of Brown and Shannon,⁶ which take the form $s = s_0(R/R_0)^{-p}$. The parameters s_0 and R_0 are the standard bond strength and bond length values of a relevant reference system; s and R are for the same atom pair in another structure and p is an empirical constant (described below). In the present study two such

relationships are needed, one for the Sn(II)–O bonds and one for the Sn(II)–Cl bonds. The total bond strength for all the bonds around a divalent tin atom provides another equation: $\Sigma s_{\text{Cl}} + \Sigma s_{\text{ox}} = 2.00$, where s_{Cl} and s_{ox} are the individual strengths for the bonds to chlorine and oxygen. With the corresponding coordination numbers N_{Cl} and N_{ox} , the equation becomes:

$$\Sigma N_i s_i = N_{\text{Cl}} s_{\text{Cl}} + N_{\text{ox}} s_{\text{ox}} = 2. \quad (1)$$

Table 1 shows that if SnO and the gas-phase SnCl₂ monomer are used as reference systems, the published^{7–16} bond lengths for a variety of crystalline systems containing Sn(II)–O and/or Sn(II)–Cl bonds satisfy eqn. (1) for chlorine and oxygen p -values of 7.0 and 4.6, respectively. Beagley *et al.*¹⁷ have recently shown that a similar treatment when applied to Mn(II)–I, Mn(II)–O and Mn(II)–P bonds satisfactorily correlates the lengths of these bonds for a range of environments. The applicability of the equations for alkali halides with varying cation coordination numbers has also been demonstrated.^{18,19}

For the tin(II) crown ether solutions in which we are interested in examining the variation of coordination numbers as well as the lengths of the bonds, the equations were

Table 1. Constraint parameters for EXAFS refinements showing agreements for known tin(II) structures.^a

(a) Reference values for Brown and Shannon equations:					
Structure	Ref.	Bond	R_0	s_0	N
SnCl ₂ (gas-phase)	8	Sn–Cl	2.345	1.00	2.00
SnO	9,10	Sn–O	2.22	0.50	4.00
(b) Agreement for known crystal structures:					
(i) structure with only Sn–O bonds [$s_{\text{ox}} = s_0(R/R_0)^{-4.6}$]					
Compound	Ref.	Distances	Bond strengths		
Sn(II)oxalate	11,12	$2 \times R_{\text{(Sn–O)}}$ at 2.23 $2 \times R_{\text{(Sn–O)}}$ at 2.39 $2 \times R_{\text{(Sn–O)}}$ at 2.88	$2s_{\text{ox}} = 0.98$ $2s_{\text{ox}} = 0.71$ $2s_{\text{ox}} = 0.30$ $\Sigma N_{\text{ox}} s_{\text{ox}} = 1.99(2.00)^b$		
(ii) structure with only Sn–Cl bonds [$s_{\text{Cl}} = s_0(R/R_0)^{-7.0}$]					
Compound	Ref.	Distances	Bond strengths		
[SnCl ₃] [–]	13	$3 \times R_{\text{(Sn–Cl)}}$ × 2.445	$3s_{\text{Cl}} = 2.24(2.00)^b$		
[SnCl ₃] [–]	14	$3 \times R_{\text{(Sn–Cl)}}$ × 2.481	$3s_{\text{Cl}} = 2.02(2.00)^b$		
CsSnCl ₃	15	$6 \times R_{\text{(Sn–Cl)}}$ × 2.75	$6s_{\text{Cl}} = 1.97(2.00)^b$		
CsSnCl ₃	16	$6 \times R_{\text{(Sn–Cl)}}$ × 2.78	$6s_{\text{Cl}} = 1.82(2.00)^b$		
(iii) structures with Sn–O and Sn–Cl bonds					
Compound	Ref.	Distances	Bond strengths		
SnCl ₂ · dioxan	7	$2 \times R_{\text{(Sn–O)}}$ at 2.527 $2 \times R_{\text{(Sn–Cl)}}$ at 2.472	$2s_{\text{ox}} = 0.55$ $2s_{\text{Cl}} \times 1.38$ $\Sigma N_i s_i = 1.93(2.00)^b$		
[Sn(18CR6)Cl] ⁺	14	$6 \times R_{\text{(Sn–O)}}$ at 2.721 ^c $1 \times R_{\text{(Sn–Cl)}}$ at 2.439 ^c	$6s_{\text{ox}} = 1.18$ $s_{\text{Cl}} = 0.76$ $\Sigma N_i s_i = 1.94(2.00)^b$		

^aWith $p_{\text{Cl}} = 7.0$ and $p_{\text{ox}} = 4.6$; distances in Å. ^bTheoretical value in parentheses. ^cOverall mean lengths for 3 examples of the [Sn(18CR6)Cl]⁺ cation.

used as an aid in constraining the least-squares refinements. This was achieved by considering the total coordination number ΣN_i of the samples, as well as the bond lengths $R_{(\text{Sn}-\text{Cl})}$ and $R_{(\text{Sn}-\text{O})}$, as *independent* variables. The *dependent* parameters, which include s_{Cl} and s_{Ox} , are then calculated from the refined bond lengths by inputting the s_0 , R_0 and p values of Table 1 into the Brown and Shannon relationship. Also dependent are the individual coordination numbers N_{Cl} and N_{Ox} because $N_{\text{Cl}} = \Sigma N_i - N_{\text{Ox}}$. This allows us to recast eqn. (1) into the form:

$$(\Sigma N_i - N_{\text{Ox}})s_{\text{Cl}} + N_{\text{Ox}}s_{\text{Ox}} = 2.00, \quad (2)$$

giving

$$N_{\text{Ox}} = (2.00 - s_{\text{Cl}}\Sigma N_i)/(s_{\text{Ox}} - s_{\text{Cl}}). \quad (3)$$

The EXAFS refinements were arranged so as to follow the conventional strategy of gas-phase electron diffraction refinement²⁰ as incorporated in the UMIST least-squares program MOLEX 85 for EXAFS curve fitting.²¹ This program contains a subroutine – DEPEND – which relates the refined independent variables (here ΣN_i , $R_{(\text{Sn}-\text{Cl})}$ and $R_{(\text{Sn}-\text{O})}$) with the appropriate parameters (s_{Cl} , s_{Ox} , N_{Cl} and N_{Ox}) through the relevant equations (see above). The DEPEND subroutine provides the means, through the least-squares algorithm, for changing both the independent variables and the dependent parameters in order to attain the best fit.

The calculations were carried out on the main-frames of the University of Manchester Regional Computing Centre, employing the EXAFS equations of Ref. 17. Data from the x-ray absorption near-edge structure (XANES) region, $E < 2.5$ Hartree, were excluded from all refinements. The EXAFS equations were parameterised by using polycrystalline dichloro(1,4-dioxan)tin(II) as the reference compound, its structural parameters being available from a crystallographic study.⁷ The computation for the 12-crown-4 containing solution used two independent sets of data simultaneously.

Results and discussion

The observed and difference EXAFS χ -curves are shown in Fig. 1. Inspection reveals that although the frequencies of the ripples on the normalised curves do not vary much, the spectra do show differing patterns of amplitudes. For example, all the curves have a deep trough and a high peak in the 3–4 Hartree region, but for the solutions containing 12-crown-4 and 15-crown-5, $|\chi(E)|$ is greater for these features, yet the curves overall are more damped; a comparison of Figs. 1b and 1d particularly demonstrates this behaviour. Table 2 expresses these differences in terms of the parameters obtained by the curve fitting and reveals a significant increase in the total coordination number ΣN_i for tin(II) in the solutions containing the crown ethers. This suggests that the latter coordinate quite strongly with

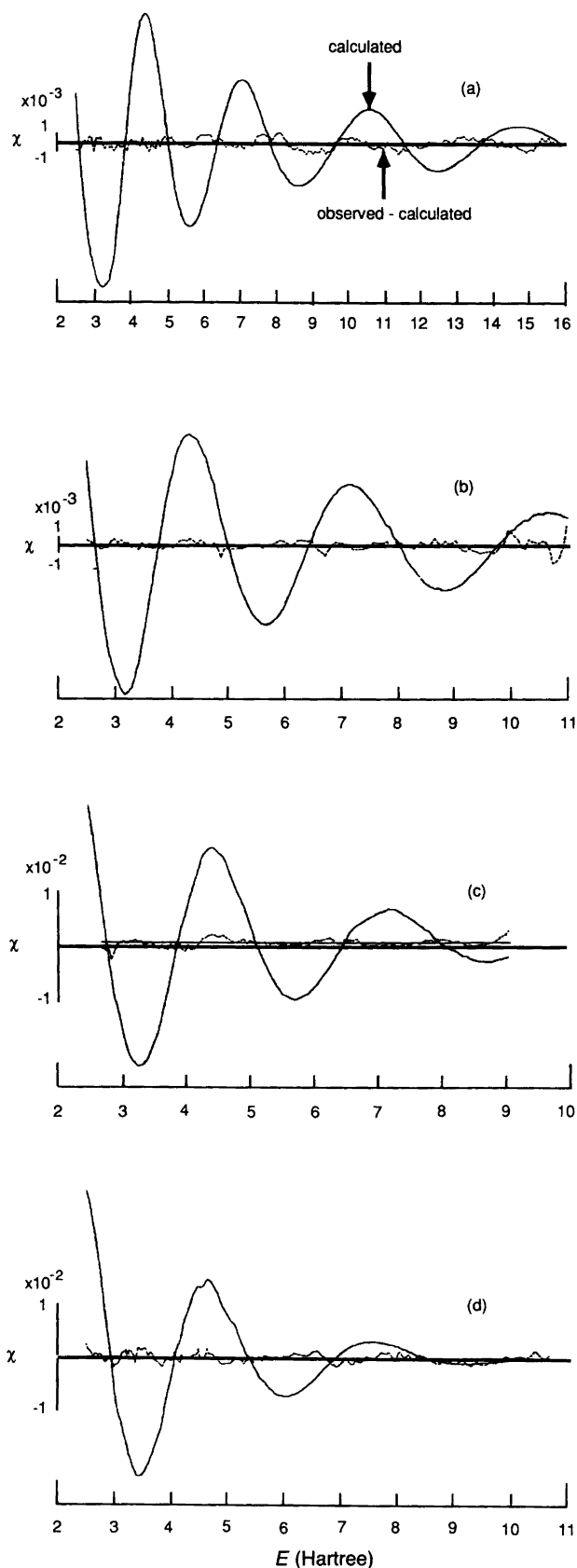


Fig. 1. EXAFS χ -curves for: (a) solid dichloro(1,4-dioxan)tin(II), reference compound and methanol solutions of (b) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (c) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} + 12\text{-crown-4}$ (d) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} + 15\text{-crown-5}$.

Table 2. Results of EXAFS curve-fitting.^a

Parameter	Solid reference ^b SnCl ₂ · dioxan	Methanol solution ^c		
		No crown	12-crown-4	15-crown-5
Data range/Hartree	2.5–16	2.5–11	2.5–9.25 ^d	2.5–11
Sn–Cl/Å	2.47(fixed)	2.47(1)	2.56(1)	2.58(1)
Sn–O/Å	2.53(fixed)	2.51(1)	2.72(1)	2.69(1)
ΣN _i	4.00(fixed)	3.6(1)	6.9(3)	8.0(2)
N _{Cl}	2.00(fixed)	2.4(dep)	1.8(dep)	1.2(dep)
N _{ox}	2.00(fixed)	1.2(dep)	5.1(dep)	6.8(dep)
σ(Sn–Cl)/Å	0.084(2)	0.084(fixed)	0.084(fixed)	0.084(fixed)
σ(Sn–O)/Å	0.10(1)	0.10(fixed)	0.10(fixed)	0.10(fixed)
Δr(Sn–Cl)/Å	0.049(6)	0.05(fixed)	0.05(fixed)	0.05(fixed)
Δr(Sn–O)/Å	0.49(1)	0.49(fixed)	0.49(fixed)	0.49(fixed)
Sn···Cl/Å	3.38(1)			
Sn···Sn/Å	4.59(fixed)			
σ(Sn···Cl)/Å	0.15(fixed)			
σ(Sn···O)/Å	0.15(fixed)			
Σr(Sn···Sn)/Å	0.47(2) ^e			
N(Sn···Cl)	2.5(3) ^e			
N(Sn···Sn)	4(1) ^e			

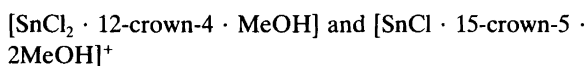
^aSee Ref. 17 for theory and definitions of σ and Δr . E.s.d.'s are in parentheses, except for fixed and dependent (= dep) parameters.

^bRef. 7. ^cSolutions contain SnCl₂ · 2H₂O; see text for compositions. ^dThis range avoids a glitch at and beyond 9.5 Hartree; mean results for two data sets are given. ^eIncludes multiple scattering component.

tin(II) in solution, with an increasing effect as the size of the crown increases. Also possibly of note is the somewhat smaller chlorine coordination of 1.2 in the case of 15-crown-5 as compared with values close to 2.0 for the other samples, which indicates that this crown ether complexes more strongly to tin(II) but at the expense of chlorine coordination.

Clearly, there must be equilibria between several species in each of the solutions, but, unlike the more extensively studied aqueous MnBr₂ solutions²² where all the components in the equilibria are octahedrally coordinated to the metal, in the Sn(II) solutions the components occur with a variety of coordination numbers. In all solutions (including aqueous MnBr₂), individual coordination numbers such as N_{Cl} and N_{ox} in the present study, will not be integers because they are averages for the several components represented by the equilibria.

The average coordination numbers obtained, however, suggest that the main species present in the 12-crown-4 and 15-crown-5 solutions are, respectively,



when each crown donates all its oxygens simultaneously; some Cl⁻ ions also appear to be present by inference. The cationic 15-crown-5 species is related to the antimony species [SbCl₃ · 15-crown-5], which has been observed crystallographically,²³ simply by the replacement of Sb by Sn and the replacement of two chlorines by solvent oxygens. Species of the type [Sn(15-crown-5)₂]²⁺ do not have a stereochemically active lone pair on tin, as shown by the Möss-

bauer studies of Herber and Carrasquillo³ on the solid complexes. Mixtures of complexes with fewer and more halogen (or oxygen) atoms simultaneously present also satisfy the average coordination numbers, as with the aqueous MnBr₂ solutions.²² The EXAFS results are thus consistent with the [Sn(15-crown-5)₂]²⁺ cation being a component in the solutions.

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References

1. Lehn, J. M. *Struct. Bonding (Berlin)* 16 (1973) 1.
2. Drew, M. G. B. and Nicholson, D. G. *J. Chem. Soc., Dalton Trans.* (1986) 1543.
3. Herber, R. H. and Carrasquillo, G. *Inorg. Chem.* 20 (1981) 3693.
4. Johansson, G. and Ohtaki, H. *Acta Chem. Scand.* 27 (1973) 643.
5. Yamaguchi, T., Lindqvist, O., Claesson, T. and Boyce, J. B. *Chem. Phys. Lett.* 93 (1982) 528.
6. Brown, I. D. and Shannon, R. D. *Acta Crystallogr., Sect. A* 29 (1973) 266.
7. Hough, E. and Nicholson, D. G. *J. Chem. Soc., Dalton Trans.* (1976) 1782.
8. B. Gershiikov, A. G., Zazorin, E. Z., Demidov, A. V. and Spiridonov, V. P. *Zh. Strukt. Khim.* 27 (1986) 36 (English edition, p. 375).

9. Pannetier, J. and Denes, G. *Acta Crystallogr., Sect. B* 36 (1980) 2763.
10. Izumi, F. *J. Solid State Chem.* 38 (1981) 381.
11. Christie, A. D., Howie, R. A. and Moser, W. *Inorg. Chim. Acta* 36 (1979) L447.
12. Gleizes, A. and Galy, J. *J. Solid State Chem.* 30 (1979) 23.
13. Stalick, J. K., Corfield, P. W. R. and Meek, D. W. *Inorg. Chem.* 12 (1973) 1668.
14. Drew, M. G. B. and Nicholson, D. G. *J. Chem. Soc., Dalton Trans.* (1986) 1543.
15. Bulanova, G. G., Podlesskaya, A. B., Soboleva, L. V. and Soklakov, A. I. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 8 (1972) 1930.
16. Barrett, J., Bird, S. R. A., Donaldson, J. D. and Silver, J. *J. Chem. Soc. A* (1971) 3105.
17. Beagley, B., McAuliffe, C. A., Pritchard, R. G. and White, E. W. *Acta Chem. Scand., Ser. A* 42 (1988) 544.
18. Beagley, B. In: Sim, G. A. and Sutton, L. E., Eds., *Molecular Structure by Diffraction Methods; Specialist Periodical Report No. 3*, The Chemical Society, London 1975, p. 52.
19. Beagley, B., Henderson, C. M. B. and Taylor, D. *Mineral. Mag.* 46 (1982) 459.
20. See e.g. Seip, H. M. In: Sim, G. A. and Sutton, L. E., Eds., *Molecular Structure by Diffraction Methods; Specialist Periodical Report No. 1*, The Chemical Society, London 1973, p. 7.
21. Beagley, B. In: Hargittai, I. and Hargittai, M., Eds., *Stereochemical Applications of Gas-Phase Electron Diffraction; Methods in Stereochemical Analysis*, VCH, New York 1988, Chap. 13.
22. Beagley, B., Gahan, B., Greaves, G. N., McAuliffe, C. A. and White, E. W. *J. Chem. Soc., Chem. Commun.* (1985) 1804.
23. Hough, E., Nicholson, D. G. and Vasudevan, A. K. *J. Chem. Soc., Dalton Trans.* (1987) 427.

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