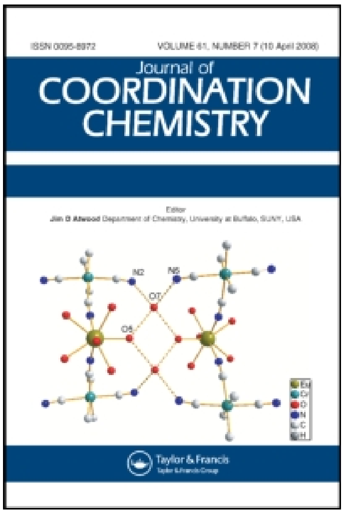

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# Reaction of Early Transition Metal Complexes With Macrocycles III. Synthesis and Structure of 18-Crown-6·I$_4$ (M = Ti, Sn)

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# REACTION OF EARLY TRANSITION METAL COMPLEXES WITH MACROCYCLES III.[†] SYNTHESIS AND STRUCTURE OF 18-CROWN-6·$MCl_4$ (M = Ti, Sn)

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18-Crown-6 reacts with either $TiCl_4$ or $SnCl_4$ in toluene to form an addition complex in which the macrocycle functions as a bidentate ligand. The two compounds are isostructural and belong to the monoclinic space group $P2_1/n$. For Ti, the cell parameters are $a$ = 10.501(6), $b$ = 18.104(5), $c$ = 10.955(5) Å, $\beta$ = 109.76(3)°, and $D_c$ = 1.55 g/cm³ for $Z$ = 4; for Sn, $a$ = 10.572(9), $b$ = 18.139(6), $c$ = 11.056(5) Å, $\beta$ = 109.16(4)°, and $D_c$ = 1.75 g/cm³. Least-squares refinement led to a final $R$ = 0.037 for 1735 observed reflections for the Ti complex, and $R$ = 0.038 for 2940 observed reflections for the Sn derivative. The M-Cl lengths range from 2.221(2)-2.285(2) Å for M = Ti, and from 2.353(2)-2.357(2) Å for M = Sn. The M-O bonds are 2.102(4) and 2.138(4) Å for M = Ti, and 2.212(4) and 2.237(4) Å for M = Sn.

**Key words:** 18-crown-6, titanium, tin, halide, x-ray

## INTRODUCTION

Despite the fact that two of the earliest reports of the metal binding properties of crown ethers concerned their complexes with transition metals,[1,2] only a fleeting interest has been further shown in the area.[3] At the same time enormous attention has been paid to the coordination chemistry of the analogous, biologically relevant nitrogen macrocycles.[4,5] The major reason for this is a combination of the directional demands of the metal *d*-orbitals and the lack of a readily available, suitably sized crown containing the four donor atoms best able to fulfil these requirements. As we have shown in previous contributions, however,[6-10] viewing these compounds as variably multidentate ligands rather than simply as macrocycles casts a new light upon their position in coordination chemistry, opening up new areas in the complexation of harder metals. We report here another transition metal complex of 18-crown-6, 18-crown-6·$TiCl_4$(**1**), in which the crown displays a rare bidentate ligating mode, and an analogous main-group metal compound, 18-crown-6·$SnCl_4$ (**2**). The latter is especially significant as, although several reports have appeared of crown complexes with Sn(II)[11] and Sn(IV)[12-16] halides, all of the latter arise through secondary sphere interactions *via* bridging water molecules.

## EXPERIMENTAL

All procedures were conducted using standard Schlenk techniques.

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[†] Part II is reference 9.
*Author for correspondence.

### *Synthesis of* **1**

Titanium tetrachloride (1.90 g, 10 mmol) was added dropwise to a solution of 18-crown-6 (2.64 g, 10 mmol) in toluene (*ca.* 50cm$^3$). Precipitation of the bright-yellow microcrystalline product resulted immediately in almost quantitative yield. A sealed tube containing the mixture was heated to 100°C for 1h and allowed to cool to room temperature, whereupon yellow air-sensitive crystals formed within 1h.

### *Synthesis of* **2**

Tin tetrachloride (1.30 g, 5 mmol) was added to a solution of 18-crown-6 (1.32 g, 5 mmol) in toluene (20 cm$^3$). Precipitation of white material occurred immediately. The reaction mixture was then heated at 100° for 2h, cooled to room temperature, and filtered to give a white microcrystalline product (in almost quantitative yield). X-ray quality, colourless crystals were obtained from a THF solution upon cooling.

### *X-ray Structure Determination for* **1**

Single crystals were mounted in thin-walled glass capillaries. Final lattice parameters as determined from the least-squares refinement of $(\sin\theta/\lambda)^2$ values for 25 reflections ($2\theta > 36°$) accurately centred on an Enraf-Nonius CAD-4 diffractometer are given in Table I. Data were collected by the $\theta$–$2\theta$ scan technique as described previously.[17] A summary of data collection and structure solution parameters is also given in Table I. The intensities were corrected for Lorentz and polarization effects. Calculations were carried out using the SHELX system of computer programs.[18] Neutral atom scattering factors were taken from reference 19 and the scattering for the Ti and Cl atoms was corrected for the real and imaginary components of anomalous dispersion using the tabulations of Cromer and Liberman.[20]

Structure solution was accomplished initially by application of the direct methods

TABLE I
Crystal data and summary of intensity data collection and structure refinement for compounds **1** and **2**

| Compound | 1 | 2 |
|---|---|---|
| Molecular weight | 454.1 | 524.8 |
| Space group | $P2_1/n$ | $P2_1/n$ |
| Cell constants | | |
| $a$, Å | 10.501(6) | 10.572(9) |
| $b$, Å | 18.104(5) | 18.139(6) |
| $c$, Å | 10.955(5) | 11.056(5) |
| $\beta$, deg | 109.76(3) | 109.16(4) |
| Cell vol, Å$^3$ | 1948 | 2003 |
| Molecules/unit cell | 4 | 4 |
| $D_c$, gcm$^{-3}$ | 1.55 | 1.75 |
| $\mu$(calc), cm$^{-1}$ | 10.1 | 18.6 |
| Radiation | Mo*Kα* | Mo*Kα* |
| Max crystal dimensions (mm) | 0.35 x 0.42 x 0.90 | 0.60 x 0.60 x 1.2 |
| Scan width, deg | $0.8 + 0.2\tan\theta$ | $0.8 + 0.2\tan\theta$ |
| Standard reflections | 500, 0120, 004 | 200, 020, 002 |
| Decay of standards | 8% | <1% |
| Reflections measured | 2790 | 3939 |
| $2\theta$ range, deg | 2–44 | 2–50 |
| Reflections considered observed ($I>3\sigma(I)$) | 1735 | 2940 |
| No. of parameters varied | 208 | 208 |
| GOF | 1.2 | 1.4 |
| $R$ | 0.037 | 0.038 |
| $R_w$ | 0.039 | 0.036 |

TABLE II
Final fractional coordinates for **1**, with estimated standard deviations in parentheses.

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Ti | 0.7012(1) | 0.13409(6) | 0.1925(1) |
| Cl(1) | 0.8761(2) | 0.1556(1) | 0.3821(2) |
| Cl(2) | 0.8168(2) | 0.0448(1) | 0.1313(2) |
| Cl(3) | 0.5058(2) | 0.1106(1) | 0.0243(2) |
| Cl(4) | 0.7548(2) | 0.2314(1) | 0.0953(2) |
| O(1) | 0.5766(4) | 0.1991(2) | 0.2681(4) |
| O(2) | 0.6245(4) | 0.0595(5) | 0.3031(4) |
| O(3) | 0.7287(4) | −0.0255(3) | 0.5345(4) |
| O(4) | 0.7275(4) | 0.1005(2) | 0.6924(4) |
| O(5) | 0.6884(4) | 0.2561(3) | 0.6894(4) |
| O(6) | 0.5699(4) | 0.3219(2) | 0.4369(4) |
| C(1) | 0.5440(9) | 0.1663(4) | 0.3722(8) |
| C(2) | 0.5308(8) | 0.0903(4) | 0.3576(9) |
| C(3) | 0.6307(7) | −0.0206(3) | 0.3042(7) |
| C(4) | 0.7461(8) | −0.0469(4) | 0.4166(7) |
| C(5) | 0.8445(6) | 0.0056(4) | 0.6271(7) |
| C(6) | 0.8070(6) | 0.0368(4) | 0.7352(6) |
| C(7) | 0.7059(6) | 0.1398(4) | 0.7955(6) |
| C(8) | 0.6205(6) | 0.2060(4) | 0.7436(6) |
| C(9) | 0.6309(7) | 0.3270(4) | 0.6634(7) |
| C(10) | 0.6549(7) | 0.3592(4) | 0.5487(6) |
| C(11) | 0.6072(7) | 0.3289(4) | 0.3249(6) |
| C(12) | 0.5287(6) | 0.2736(3) | 0.2291(6) |

TABLE III
Final fractional coordinates for **2**, with estimated standard deviations in parentheses.

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Sn | 0.19383(4) | 0.13582(2) | 0.18878(4) |
| Cl(1) | 0.3713(2) | 0.1602(1) | 0.3820(2) |
| Cl(2) | 0.3184(2) | 0.0413(1) | 0.1283(2) |
| Cl(3) | −0.0022(2) | 0.1091(1) | 0.0228(2) |
| Cl(4) | 0.2498(2) | 0.2314(1) | 0.0953(2) |
| O(1) | 0.0679(4) | 0.2016(2) | 0.2682(4) |
| O(2) | 0.1208(4) | 0.0597(5) | 0.3073(4) |
| O(3) | 0.2263(5) | −0.0258(3) | 0.5339(4) |
| O(4) | 0.2258(4) | 0.0976(3) | 0.6908(4) |
| O(5) | 0.1825(4) | 0.2529(3) | 0.6839(5) |
| O(6) | 0.0633(4) | 0.3216(3) | 0.4370(4) |
| C(1) | 0.021(1) | 0.1663(5) | 0.358(1) |
| C(2) | 0.035(1) | 0.0926(5) | 0.366(1) |
| C(3) | 0.1271(8) | −0.0196(3) | 0.3087(7) |
| C(4) | 0.2438(9) | −0.0457(4) | 0.4160(7) |
| C(5) | 0.3417(7) | 0.0032(4) | 0.6272(7) |
| C(6) | 0.3050(7) | 0.0351(4) | 0.7342(7) |
| C(7) | 0.2040(7) | 0.1381(4) | 0.7932(6) |
| C(8) | 0.1153(6) | 0.2025(4) | 0.7393(6) |
| C(9) | 0.1224(7) | 0.3235(4) | 0.6612(7) |
| C(10) | 0.1467(87 | 0.3575(4) | 0.5487(6) |
| C(11) | 0.0999(7) | 0.3300(4) | 0.3258(7) |
| C(12) | 0.0215(6) | 0.2757(4) | 0.2300(6) |

program MULTAN,[21] which revealed the Ti and Cl positions. Difference Fourier maps phased upon these readily gave the coordinates of the remaining non-hydrogen atoms, all of which were subsequently treated with anisotropic thermal parameters. All the hydrogen atoms except those attached to C(1) and C(2) were located, assigned an isotropic temperature factor of 6.3 Å$^2$, and allowed to ride upon the bonded carbon atoms. Those for C(1) and C(2) were treated in a similar fashion after being geometrically positioned. Further refinement converged at reliability values of $R = \Sigma|F_o| - |F_c|/\Sigma|F_o| = 0.037$, $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2\}^{1/2} = 0.039$. A final difference Fourier showed no feature greater than 0.3 e/Å$^3$. The weighting scheme was

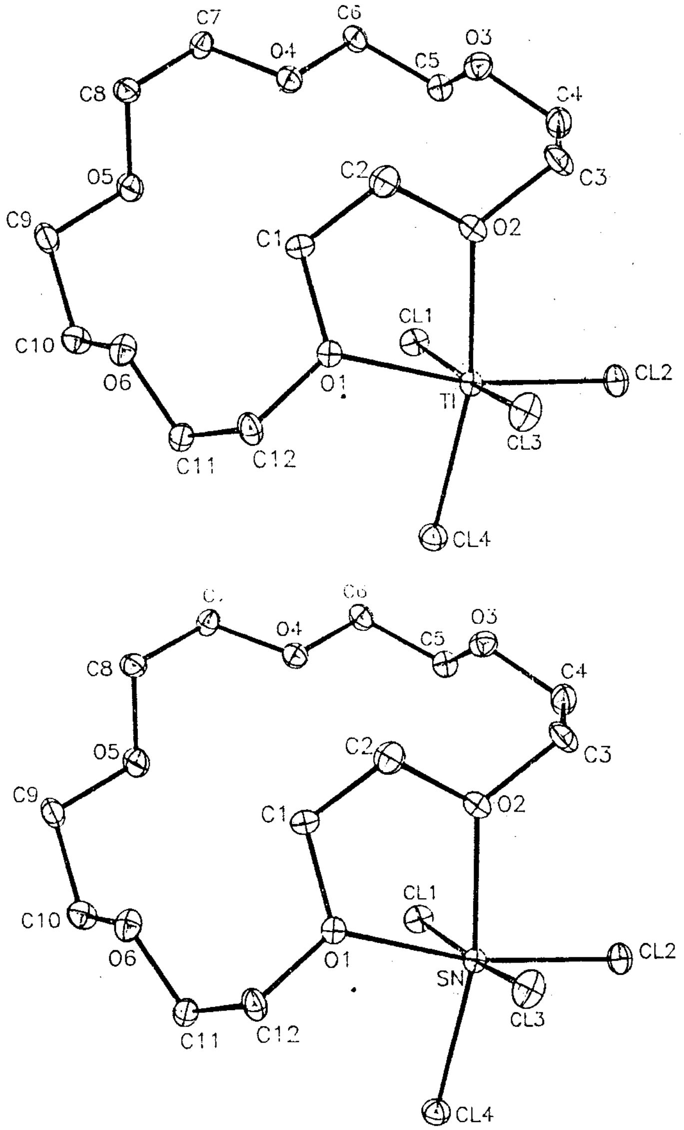

FIGURE 1 (a): Molecular structure of 18-crown-6·TiCl$_4$. (b): 18-crown-6·SnCl$_4$.

based upon unit weights and no systematic variation of $w(|F_o| - |F_c|)^2$ *vs* $F_o$ or $(\sin\theta/\lambda)$ was observed. The final values of the positional parameters are given in Table II. Tables of anisotropic thermal parameters, hydrogen atom coordinates and structure factors are available as supplementary material from the Editor.

### *X-ray Structure Determination for* **2**

A summary of data collection parameters is given in Table I. As the molecule is isostructural to **1**, the atomic coordinates for the latter were used as the starting values in the structure solution. Refinement as above converged at $R = 0.038$ and $R_w = 0.036$. Positional parameters are given in Table III. Supplementary data are available from the Editor.

## RESULTS AND DISCUSSION

Representative views of the compounds are given in Figure 1, and relevant bond lengths and angles in Table IV. The most immediate point of interest is the conformation of the crown ether, which is bent away from the metallic species by rather severe distortions about the O(2)-C(3) and O(1)-C(12) bonds (torsion angles are given in Table V). This

TABLE IV
Bond lengths (Å) and Angles (°) for 18-crown-6·$MCl_4$ (M=Ti, Sn) with estimated standard deviations in parentheses.

| Bond | M=Ti (Compound **1**) | M=Sn (Compound **2**) |
|---|---|---|
| M-Cl(1) | 2.285(2) | 2.355(2) |
| M-Cl(2) | 2.229(2) | 2.353(2) |
| M-Cl(3) | 2.279(2) | 2.357(2) |
| M-Cl(4) | 2.221(2) | 2.354(2) |
| M-O(1) | 2.102(4) | 2.212(4) |
| M-O(2) | 2.138(4) | 2.237(4) |
| O-C (range) | 1.400(7)-1.453(7) | 1.405(8)—1.440(7) |
| O-C (average) | 1.42(1) | 1.42(1) |
| C-C (range) | 1.382(9)-1.485(9) | 1.34(1)-1.491(9) |
| C-C (average) | 1.46(2) | 1.46(2) |
| *Angle* | | |
| Cl(1)-M-Cl(2) | 92.97(8) | 93.68(7) |
| Cl(1)-M-Cl(3) | 170.73(8) | 168.16(6) |
| Cl(1)-M-Cl(4) | 92.53(7) | 93.32(6) |
| Cl(2)-M-Cl(3) | 92.60(7) | 93.44(6) |
| Cl(2)-M-Cl(4) | 100.63(8) | 102.07(6) |
| Cl(3)-M-Cl(4) | 93.72(8) | 94.42(6) |
| Cl(1)-M-O(1) | 87.6(1) | 86.5(1) |
| Cl(2)-M-O(1) | 167.5(1) | 165.7(1) |
| Cl(3)-M-O(1) | 85.4(1) | 84.3(1) |
| Cl(4)-M-O(1) | 91.9(1) | 92.2(1) |
| Cl(1)-M-O(2) | 86.2(1) | 84.8(1) |
| Cl(2)-M-O(2) | 92.9(1) | 93.0(1) |
| Cl(3)-M-O(2) | 86.1(1) | 85.4(1) |
| Cl(4)-M-O(2) | 166.4(1) | 164.9(1) |
| O(1)-M-O(2) | 74.6(2) | 72.8(1) |
| C-O-C (range) | 112.5(5)—116.9(5) | 112.3(5)-117.8(3) |
| C-O-C (average) | 115(1) | 115(1) |
| O-C-C (range) | 107.6(5)-111.1(5) | 107.5(5)-116.3(7) |
| O-C-C (average) | 110(2) | 111(2) |

TABLE V
Torsion angles (°) around the crown in compound **1**.

| Atoms | Angle (±1°) |
|---|---|
| O(1) C(1) C(2) O(2) | 35 |
| C(1) C(2) O(2) C(3) | 171 |
| C(2) O(2) C(3) C(4) | −99 |
| O(2) C(3) C(4) O(3) | 63 |
| C(3) C(4) O(3) C(5) | −134 |
| C(4) O(3) C(5) C(6) | 171 |
| O(3) C(5) C(6) O(4) | −71 |
| C(5) C(6) O(4) C(7) | −171 |
| C(6) O(4) C(7) C(8) | −179 |
| O(4) C(7) C(8) O(5) | −65 |
| C(7) C(8) O(5) C(6) | −169 |
| C(8) O(5) C(9) C(10) | −148 |
| O(5) C(9) C(10) O(6) | 73 |
| C(9) C(10) O(6) C(11) | −162 |
| C(10) O(6) C(11) C(12) | 167 |
| O(6) C(11) C(12) O(1) | −73 |
| C(11) C(12) O(1) C(1) | −106 |
| C(12) O(1) C(1) C(2) | 152 |

serves to relieve the strain caused by the bidentate coordination and allows the rest of the crown to adopt its preferred geometry.[22] This is in stark contrast to that observed in the complex 18-crown-6·$TiCl_3$·$H_2O$ in which the portion of the crown not bound directly to the titanium bends back towards the metal species, due to secondary interactions between the macrocyclic oxygen atoms and the coordinated water molecule.[9]

The bond lengths about the titanium and the tin complexes reflect this strain, the bonds to the oxygens being rather longer than might be expected. Indeed those to titanium are comparable to those seen in the 18-crown-6·$TiCl_3$·$H_2O$ complex despite the increase in oxidation number of the metal (2.102(4) and 2.138(4) Å in compound **1** compared to 2.123(8) and 2.154(9) Å for the complex with ligated $H_2O$[9]). That this is not due to any other possible effects is demonstrated by the expected shortening of the Ti–Cl bonds from 2.350(9) and 2.225(2) Å for those chlorine atoms *cis*- to an oxygen atom. Similarly, the Sn–Cl distances in compound **2** compare favourably with those in the literature (2.355(2) Å average, compared to 2.38(1) Å in $SnCl_4$,[23] 2.395(3) Å in 18-crown-6·$SnCl_4$·$H_2O$[14] and 2.370(12) Å in $SnCl_4(SeOCl_2)_2$,[24] whereas the Sn–O distances are considerably longer (2.212(4) and 2.237(4) A in compound **2** compared to 2.110(8), 2.114(6), and 2.115(12) Å, respectively, for the above-mentioned compounds). In both 1 and 2, the $MCl_4$ group is slightly distorted towards the crown, reflecting the constrained O(1)–M–O(2) angle of approximately 74°.

Attempts at alkylating compound **1** with a variety of reagents produced products stable only at low temperatures (*ca.* -78°C). Thus the coordination of the macrocycle does not stabilize Ti–C bonds in $TiR_4$.[25]

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