

Reaction of Early Transition Metal Complexes with Macrocycles. II. Synthesis and Structure of $\text{TiCl}_3(\text{H}_2\text{O}) \cdot 18\text{-Crown-6}$, a Compound with a Unique Bidentate Bonding Mode for the 18-Crown-6 Molecule

SIMON G. BOTT, ULRICH KYNAST, and JERRY L. ATWOOD*

Department of Chemistry, University of Alabama, University, AL 35486 U.S.A.

(Received: 12 November 1985)

Abstract. 18-crown-6 reacts with TiCl_3 in CH_2Cl_2 to form a complex in which the crown ether functions as a tridentate ligand. Addition of moist hexane affords a molecular complex in which the crown ether functions as a bidentate ligand. A water molecule is bonded directly to the titanium atom and is further hydrogen bonded to three of the oxygen atoms of the crown. The deep blue crystals of the CH_2Cl_2 adduct belong to the monoclinic space group $P2_1/n$ with $a = 13.481(8)$, $b = 8.021(5)$, $c = 21.425(9)$ Å, $\beta = 97.32(5)^\circ$, and $\rho_{\text{calc}} = 1.51 \text{ g cm}^{-3}$ for $Z = 4$. Refinement led to a conventional R value of 0.040 based on 873 observed reflections. The Ti—O bond distances for the crown oxygen atoms are 2.123(8) and 2.154(9) Å, while the oxygen atom of the water molecule is bonded at 2.072(8) Å. The octahedral coordination sphere of the titanium atom is completed by the three chlorine atoms at distances of 2.340(5), 2.352(4), and 2.373(4) Å.

Key words: Crown ether, early transition metal, hydrogen bonding, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82034 (10 pages).

1. Introduction

It has been recently shown that AlCl_3 reacts with crown ethers to form complexes of the type $[\text{AlCl}_2 \cdot \text{crown ether}] [\text{AlCl}_4]$ [1]. These salts exhibit the liquid clathrate effect [2] and the crown ether functions as a tetradentate ligand in the octahedral array about the aluminum atom. It seemed possible that TiCl_4 or TiCl_3 would function in the same manner. There were no data in the literature to allow the assessment of this idea, since the reaction of early transition metal complexes with crown ethers has been largely ignored [3]. This is particularly surprising given the level of activity concerning the late transition metals [4,5]. In this contribution we show that the reaction of TiCl_3 with 18-crown-6 leads initially to the formation of a complex in which the 18-crown-6 molecule functions as a tridentate ligand. Addition of moist hexane to a solution of this compound in CH_2Cl_2 produces the title complex in which the 18-crown-6 functions as a bidentate ligand.

* Author for correspondence.

2. Experimental

Manipulations were carried out either in an inert atmosphere glove box or using Schlenk techniques.

2.1. SYNTHESIS OF $\text{TiCl}_3(\text{H}_2\text{O}) \cdot 18\text{-crown-6}$

1.73 g of TiCl_3 (0.0112 mol) and 8.80 g of 18-crown-6 (0.0336 mol) were thoroughly mixed in a 100 ml flask. The mixture was stirred and heated to 120°C for 8 h, then cooled to room temperature and 60 ml of toluene were added. After refluxing for 2 h the raw product was filtered and washed with two 30 ml portions of toluene. The solid residue was then stirred with 60 ml of CH_2Cl_2 for 15 min, and the resulting violet solution was separated from the insoluble residue.

Blue $\text{TiCl}_3(\text{H}_2\text{O}) \cdot 18\text{-crown-6} \cdot \text{CH}_2\text{Cl}_2$ can be crystallized in low yield (15% rel. to TiCl_3) from this solution by addition of a layer of insufficiently dried n-hexane, whereas yellow $\text{TiCl}_3 \cdot 18\text{-crown-6}$ can be obtained upon cooling (-10°C) after a few days (yield $\sim 45\%$ rel. to TiCl_3).

IR-data (crown omitted) of $\text{TiCl}_3(\text{H}_2\text{O}) \cdot 18\text{-crown-6} \cdot \text{CH}_2\text{Cl}_2$ [6],

3380 cm^{-1} medium, broad, $\nu_{\text{as}}(\text{H}_2\text{O})$,

3238 cm^{-1} medium broad, $\nu_{\text{s}}(\text{H}_2\text{O})$,

1610 cm^{-1} strong, $\delta(\text{H}_2\text{O})$,

346 cm^{-1} very strong, broad, $\nu(\text{TiCl}_3)$

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT FOR $\text{TiCl}_3(\text{H}_2\text{O}) \cdot 18\text{-crown-6} \cdot \text{CH}_2\text{Cl}_2$

Single crystals of the compound were sealed under N_2 in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of the angular settings of 25 reflections ($\theta > 20^\circ$) accurately centered on the diffractometer are given in Table I. The space group was found to be $P2_1/n$.

Table I. Crystal data for $\text{TiCl}_3(\text{H}_2\text{O}) \cdot 18\text{-crown-6} \cdot \text{CH}_2\text{Cl}_2$

Mol wt	521.6	Radiation	$\text{MoK}\alpha$
Space group	$P2_1/n$	max cryst dimens, mm	$0.20 \times 0.15 \times 0.20$
Cell constants		scan width, deg	$0.8 + 0.2 \tan \theta$
a , Å	13.481(8)	std reflections	200, 020, 002
b , Å	8.021(5)	variation of stds	$< 4\%$
c , Å	21.425(9)	reflectns measd	2528
β , deg	97.32(5)	2θ range	1–40
Cell vol, Å ³	2298	obsd reflectns	873
mol/unit cell	4	no. of par varied	140
$\rho(\text{calc})$, g cm ⁻³	1.51	R	0.040
$\mu(\text{calc})$, cm ⁻¹	9.84	R_w	0.040

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ - 2θ scan technique. The method has been previously described [7]. A summary of data collection parameters is also given in Table I. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Calculations were carried out using the SHELX system of programs [8].

The structure was solved by the application of the direct method program MULTAN [9]. Subsequent difference Fourier maps allowed the location of all non-hydrogen atoms. The interpretation was made slightly more difficult by the presence of one CH_2Cl_2 molecule of solvation in the asymmetric unit. The shortage of observed data due to the relatively poor scattering ability of the crystal did not permit full anisotropic refinement. The titanium atom, all the chlorine atoms (including those of the CH_2Cl_2), and the water oxygen were treated with anisotropic thermal parameters. The atoms of the 18-crown-6 unit were refined with isotropic thermal temperature factors. The hydrogen atoms associated with the crown ether moiety were placed in calculated positions 1.00 Å from the bonded carbon atom. The hydrogen atoms of the water molecule and of the solvent molecules were located on a difference Fourier map, but were not refined. The structure was refined in this fashion to a final R value of 0.040. No unaccounted electron density was noted on the final difference Fourier map. The final values of the positional parameters are given in Table II.

Table II. Final fractional coordinates for $\text{TiCl}_3(\text{H}_2\text{O}) \cdot 18\text{-crown-6} \cdot \text{CH}_2\text{Cl}_2$

Atom	x/a	y/b	z/c
Ti	0.5441(2)	0.5370(3)	0.6708(1)
Cl(1)	0.6897(3)	0.5632(5)	0.6226(2)
Cl(2)	0.4387(3)	0.6951(4)	0.5974(2)
Cl(3)	0.5855(3)	0.7596(4)	0.7423(2)
Cl(4)	0.793(2)	0.089(3)	0.537(1)
Cl(5)	0.9188(4)	0.3821(8)	0.5425(2)
O(1)	0.5208(6)	0.305(1)	0.6205(4)
O(2)	0.6090(6)	0.354(1)	0.7351(4)
O(3)	0.4831(7)	0.356(1)	0.8326(4)
O(4)	0.2814(6)	0.321(1)	0.7888(4)
O(5)	0.2230(6)	0.376(1)	0.6595(4)
O(6)	0.3282(6)	0.186(1)	0.5757(4)
O(7)	0.4170(5)	0.470(1)	0.7099(3)
C(1)	0.556(1)	0.159(2)	0.6555(7)
C(2)	0.630(1)	0.196(2)	0.7066(7)
C(3)	0.6456(9)	0.369(2)	0.8017(5)
C(4)	0.5791(9)	0.281(2)	0.8402(6)
C(5)	0.4156(9)	0.279(2)	0.8694(6)
C(6)	0.3152(9)	0.348(2)	0.8527(6)
C(7)	0.190(1)	0.399(2)	0.7661(6)
C(8)	0.154(1)	0.341(2)	0.7027(6)
C(9)	0.186(1)	0.337(2)	0.5956(6)
C(10)	0.271(1)	0.327(2)	0.5566(6)
C(11)	0.4086(9)	0.161(2)	0.5412(6)
C(12)	0.4934(9)	0.280(2)	0.5544(6)
C(13)	0.862(6)	0.24(2)	0.583(3)

3. Results and Discussion

TiCl_3 was contacted with 18-crown-6 using an excess of the crown ether as the reaction medium. Treatment with CH_2Cl_2 yielded a dark violet solution from which yellow cuboids were obtained. The infrared spectrum exhibits two significant bands: 368 cm^{-1} , strong $\nu_s \text{TiCl}_3(A_1)$; 325 cm^{-1} , very strong $\nu_{as} \text{TiCl}_3(E)$. These show that the local symmetry at the titanium atom is doubtless C_{3v} , which in turn implies a tridentate coordination mode of the 18-crown-6 molecule. Thus far attempts to grow crystals suitable for an X-ray analysis have been unsuccessful. However during one attempt, water was inadvertently added during the recrystallization process in the form of insufficiently dried hexane. Deep blue, well-formed crystals of the title compound were obtained.

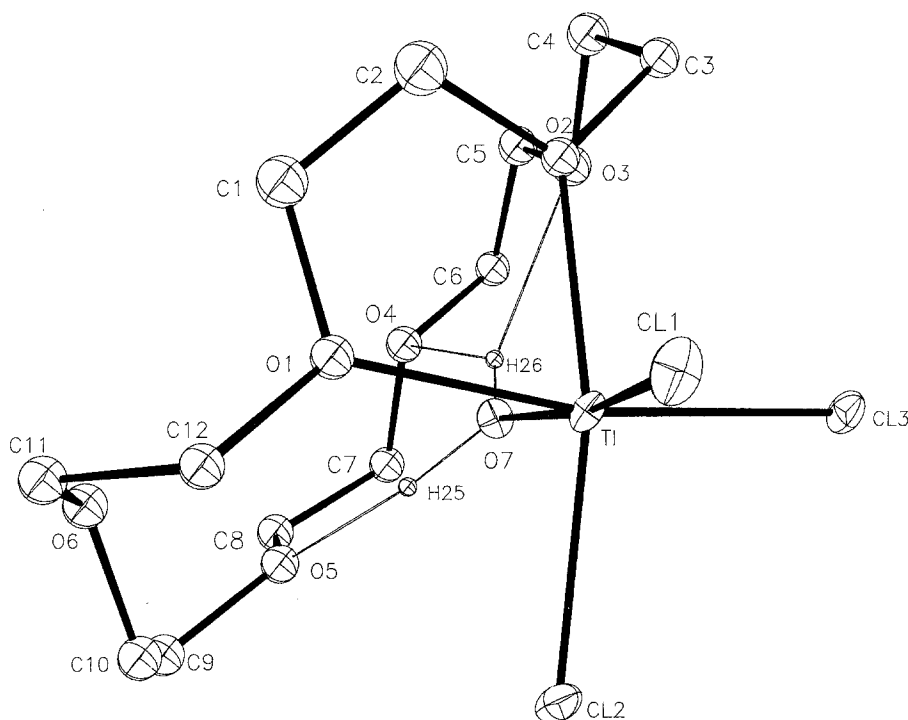


Fig. 1. Molecular structure and numbering scheme for $\text{TiCl}_3(\text{H}_2\text{O}) \cdot 18\text{-crown-6}$.

The structure of the compound, Figure 1, shows interesting features. The titanium coordination sphere is composed of three chlorine atoms, an oxygen from the water molecule, and two oxygens from the crown ether moiety. Relevant bond distances and angles are given in Table III. The water molecule is further hydrogen bonded to three oxygen atoms of the crown ether. Only O(6) is not bonded to the titanium-containing moiety in some direct fashion.

The effect of the intramolecular hydrogen bonding on the configuration of the molecule is best illustrated with reference to the structure of $\text{TiCl}_4 \cdot 18\text{-crown-6}$ [10]. The latter exhibits a bidentate bonding mode of the 18-crown-6, but the sixth position is filled by a Cl instead of the H_2O . The difference in oxidation states of the titanium atoms only affects the bond

Table III. Selected bond lengths (Å) and angles (°) for $\text{TiCl}_3(\text{H}_2\text{O}) \cdot 18\text{-crown-6} \cdot \text{CH}_2\text{Cl}_2$

Atoms	Distance	Atoms	Distance
Ti—Cl(1)	2.340(5)	Ti—Cl(2)	2.352(4)
Ti—Cl(3)	2.373(4)	Ti—O(1)	2.154(9)
Ti—O(2)	2.123(8)	Ti—O(7)	2.072(8)
O(1)—C(1)	1.44(2)	O(1)—C(12)	1.43(1)
O(2)—C(2)	1.46(2)	O(2)—C(3)	1.45(1)
O(3)—C(4)	1.42(2)	O(3)—C(5)	1.42(2)
O(4)—C(6)	1.40(1)	O(4)—C(7)	1.42(2)
O(5)—C(8)	1.42(2)	O(5)—C(9)	1.43(1)
O(6)—C(10)	1.40(2)	O(6)—C(11)	1.40(2)
C(1)—C(2)	1.42(2)	C(3)—C(4)	1.47(2)
C(5)—C(6)	1.46(2)	C(7)—C(8)	1.46(2)
C(9)—C(10)	1.50(2)	C(11)—C(12)	1.49(2)

Atoms	Angle	Atoms	Angle
Cl(1)—Ti—Cl(2)	97.2(2)	Cl(1)—Ti—Cl(3)	94.4(2)
Cl(2)—Ti—Cl(3)	95.7(1)	Cl(1)—Ti—O(1)	86.2(3)
Cl(2)—Ti—O(1)	95.4(2)	Cl(3)—Ti—O(1)	168.7(3)
Cl(1)—Ti—O(2)	92.8(3)	Cl(2)—Ti—O(2)	166.0(3)
Cl(3)—Ti—O(2)	93.2(2)	O(1)—Ti—O(2)	75.5(3)
Cl(1)—Ti—O(7)	170.1(3)	Cl(2)—Ti—O(7)	87.1(2)
Cl(3)—Ti—O(7)	94.1(2)	O(1)—Ti—O(7)	84.4(3)
O(2)—Ti—O(7)	81.5(3)	Ti—O(1)—C(1)	115.3(7)
Ti—O(1)—C(12)	128.2(7)	C(1)—O(1)—C(12)	115(1)
Ti—O(2)—C(2)	114.6(7)	Ti—O(2)—C(3)	129.9(7)
C(2)—O(2)—C(3)	115.0(9)	C(4)—O(3)—C(5)	113(1)
C(6)—O(4)—C(7)	115(1)	C(8)—O(5)—C(9)	114.0(9)
C(10)—O(6)—C(11)	113(1)	O(1)—C(1)—C(2)	113(1)
O(2)—C(2)—C(1)	110(1)	O(2)—C(3)—C(4)	111(1)
O(3)—C(4)—C(3)	110(1)	O(3)—C(5)—C(6)	110(1)
O(4)—C(6)—C(5)	111(1)	O(4)—C(7)—C(8)	110(1)
O(5)—C(8)—C(7)	112(1)	O(5)—C(9)—C(10)	110(1)
O(6)—C(10)—C(9)	108(1)	O(6)—C(11)—C(12)	116(1)
O(1)—C(12)—C(11)	112(1)		

lengths (and even then by *ca.* 0.1 Å). However, as is illustrated by Figure 2, the nonbonded portion of the crown ether is displaced well away from the titanium atom in $\text{TiCl}_4 \cdot 18\text{-crown-6}$.

Metrical evidence for the hydrogen bonding may also be noted. With the one between O(5) and O(7), the O(5)···O(7) separation is 2.80(1) Å, and the O(5)···H(25) length is 1.8 Å. Both of these values are near the norm [11]. The situation is more complicated for H(26), since it is bonded to two crown ether oxygen atoms. The approaches are O(3)···O(7), 2.82(1), and O(4)···O(7), 2.90(1) Å. The O(3) and O(4) distances to H(26) are 2.1 and 2.2 Å, respectively.

Thus, the 18-crown-6 moiety has interesting and varied ways to interact with early transition metal complexes. In later parts of this series it will be seen that this area of macrocycle chemistry is rich indeed. It must also be noted that no evidence of ion pair formation which could give rise to a liquid clathrate effect was observed.

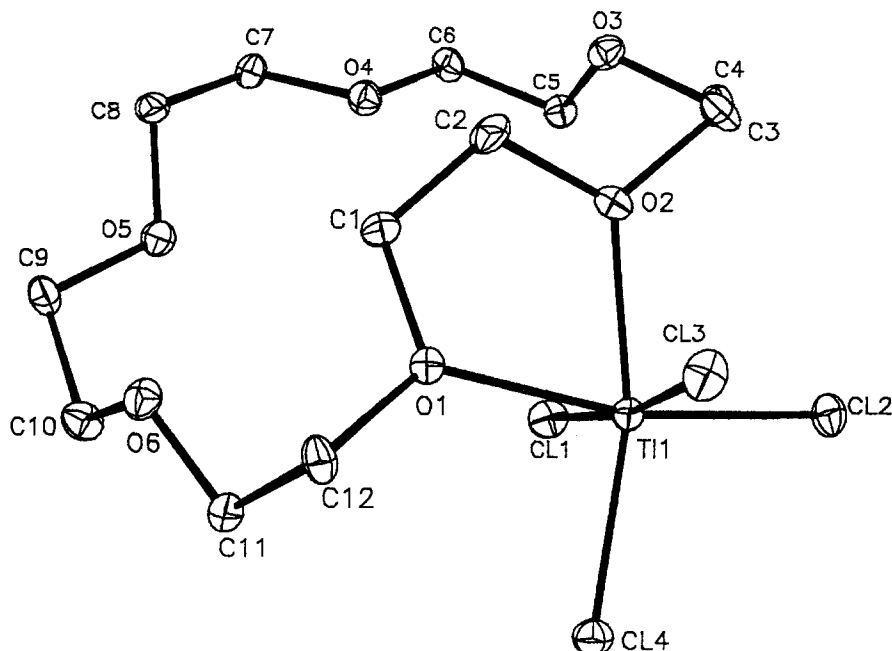


Fig. 2. Molecular structure for $\text{TiCl}_4 \cdot 18\text{-crown-6}$ [6].

Acknowledgement

We are grateful to the National Science Foundation for support of this work.

References

1. S. G. Bott, H. Elgamel, and J. L. Atwood: unpublished results, but see also S. G. Bott, H. Elgamel, and J. L. Atwood: *J. Am. Chem. Soc.* **107**, 1796 (1985) and J. L. Atwood, H. Elgamel, G. H. Robinson, S. G. Bott, J. A. Weeks, and W. E. Hunter: *J. Incl. Phenom.* **2**, 367 (1984).
2. J. L. Atwood: *Inclusion Compounds*, vol. I (eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol), pp. 395–426, Academic Press, London (1984).
3. ZrCl_4 actually reacts with 18-crown-6, effecting an opening of the macrocyclic ring. See Part I, H. Prinz, S. G. Bott, and J. L. Atwood: *J. Am. Chem. Soc.*, in press.
4. T. Sakurai, K. Kobayashi, S. Tsuboyama, Y. Kohno, N. Azuma, and K. Ishizu: *Acta Crystallogr.* C39, 206 (1983) and Y. Li, H. Tomada, K. Tajima, K. Ishizu, and N. Azuma: *Chem. Lett.*, 1961 (1985).
5. P. G. Jones, T. Gries, H. Grutzmacher, H. W. Roesky, J. Schimkowiak, and G. M. Sheldrick: *Angew. Chem. Int. Ed. Engl.* **23**, 376 (1984).
6. Spectra were taken as nujol mulls and recorded on a Perkin-Elmer 283 B infrared spectrometer.
7. J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter: *J. Chem. Soc., Dalton Trans.* 45 (1979).
8. SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick (1976).
9. G. Germain, P. Main, and M. M. Woolfson: *Acta Crystallogr.* A27, 368 (1971).
10. S. G. Bott, H. Prinz, and J. L. Atwood: unpublished results.
11. W. C. Hamilton and J. A. Ibers: *Hydrogen Bonding in Solids*, p. 15, Benjamin, New York (1964).