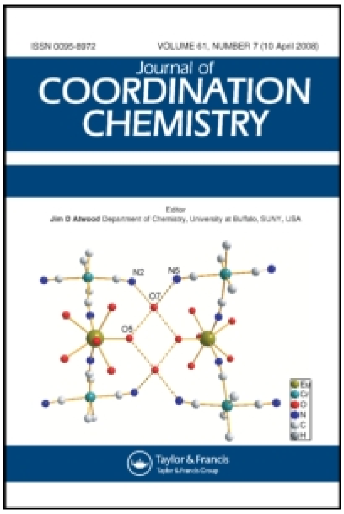

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# COMMUNICATION

# PREPARATION AND STRUCTURE OF THE $[YbCl_2 \cdot 15\text{-CROWN-5}]^+$ CATION, AN EXAMPLE OF SEVEN-COORDINATE YTTERBIUM

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The complex $[YbCl_2 \cdot 15\text{-crown-5}][AlCl_2Me_2]$ has been prepared by the reaction of $YbCl_3$, 15-crown-5, and $AlMe_3$ (1:1:4) in toluene. The colourless, air-sensitive crystals belong to the orthorhombic space group *Pnma* with $a = 11.313(7)$, $b = 10.907(5)$, $c = 17.716(7)$ Å, and $D_c = 1.81$ g cm$^{-3}$ for $Z = 4$. The structure was refined to $R = 0.048$ based on 1502 observed reflection. The Yb atom is displaced 0.20 Å from the plane of the crown ether, and the Yb–O bond distance range from 2.23–2.32 Å.

**Keywords:** ytterbium, crown ether, liquid clathrate, synthesis, structure.

## INTRODUCTION

Major advances in the organometallic chemistry of the lanthanides have followed the realization of new ligand systems through which the special properties of these elements are manifested. Thus, the cyclopentadienyl (Cp) group gave rise to most of organolanthanide chemistry until the advent of the bulky pentamethylcyclopentadienyl ligand and related systems in the late 1970's. Intermixed have been a few studies of cyclooctatetraenyl and homoleptic alkyl complexes. Even these few basic systems have afforded the development of a rich area of organometallic endeavour.[1] A major goal of our chemistry has been the utilization of a macrocycle bonded to a lanthanide so as to sterically and/or electronically modify the properties of the metal. Once in hand the complex should be amenable to classic organometallic synthetic reactions. Crown ethers are the most readily available of the oxygen-containing macrocycles, and a substantial coordination chemistry with the lanthanides already exists.[2] Unfortunately, existing complexes suffer from one of two faults; they contain water bound in some fashion, or they do not contain a metal-bound ligand which is easily replaceable by an organic group (*i.e.*, the replacement of a halide by an alkyl group). In this contribution we reveal the existence of a complex which overcomes both of these problems, $[YbCl_2 \cdot 15\text{-crown-5}][AlCl_2Me_2]$.[3] In addition, it presents the first instance of the coordination number seven for $Yb^{3+}$.

## EXPERIMENTAL

All procedures were conducted using standard Schlenk or dry box techniques. $YbCl_3$ (0.005 mol) was added to a solution of 15-crown-5 (0.005 mol) and $AlMe_3$ (0.020 mol, an excess) in toluene. The mixture was heated at 80°C in a sealed tube for 12 h. Two liquid layers[4] and a pyrophoric green solid resulted.[5] The lower liquid layer contained the title compound in *ca.* 20% yield. Larger, colourless diffraction-quality crystals were obtained

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TABLE I
Final fractional coordinates for $[YbCl_2 \cdot 15\text{-crown-}5][AlCl_2Me_2]$.

| Atom | x/a | y/b | z/c |
|---|---|---|---|
| Yb | 0.09061(6) | 0.2500 | 0.37825(4) |
| Al | −0.0103(5) | 0.2500 | 0.8731(4) |
| Cl(1) | 0.0773(5) | 0.2500 | 0.5207(3) |
| Cl(2) | 0.0975(5) | 0.2500 | 0.2353(3) |
| Cl(3) | 0.1103(6) | 0.2500 | 0.9700(4) |
| Cl(4) | 0.1058(7) | 0.2500 | 0.7743(4) |
| O(1) | −0.112(1) | 0.2500 | 0.3636(9) |
| O(2) | 0.031(1) | 0.055(1) | 0.3819(9) |
| O(3) | 0.251(1) | 0.128(1) | 0.3800(8) |
| C(1) | −0.167(1) | 0.144(2) | 0.389(1) |
| C(2) | −0.085(2) | 0.028(2) | 0.357(1) |
| C(3) | 0.106(2) | −0.036(2) | 0.359(1) |
| C(4) | 0.237(2) | 0.010(2) | 0.384(2) |
| C(5) | 0.359(1) | 0.179(2) | 0.396(2) |
| C(6) | −0.099(1) | 0.406(1) | 0.875(1) |

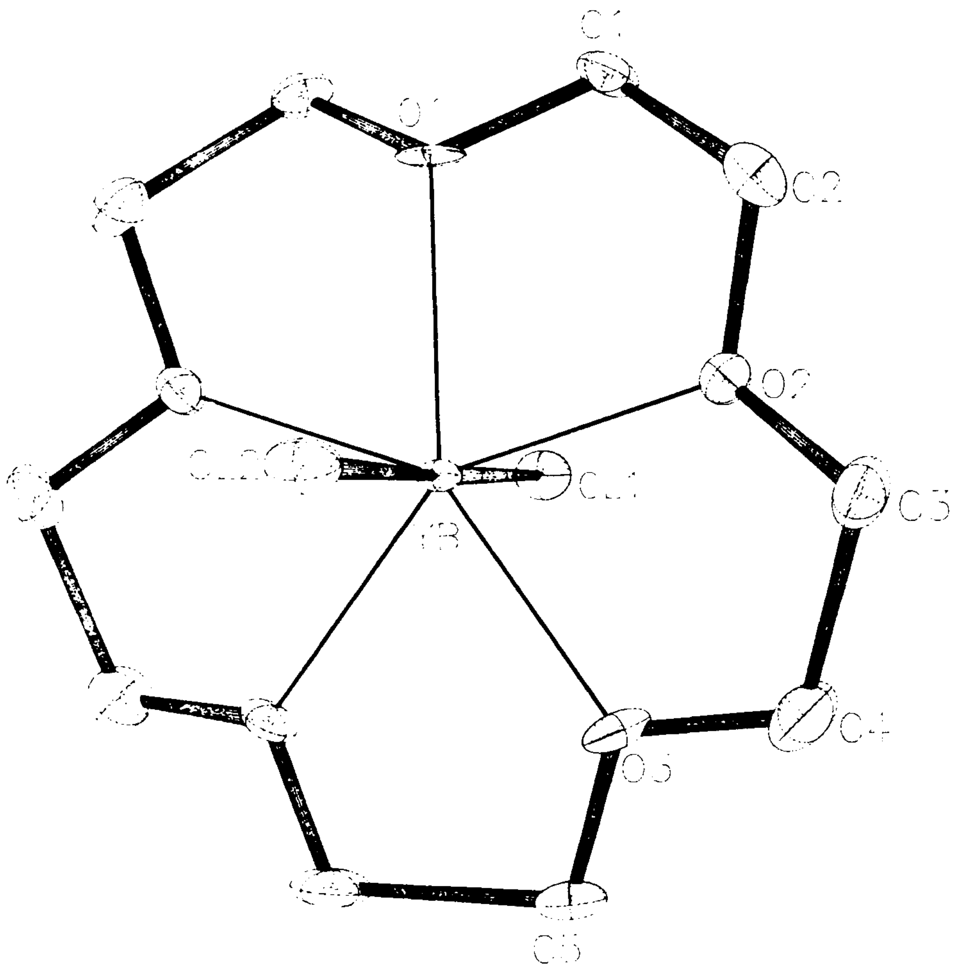

FIGURE 1 Structure of the $[YbCl_2 \cdot 15\text{-crown-}5]^+$ cation. A crystallographic mirror plane contains the Yb, both Cl atoms, and O(1).

by cooling the liquid clathrate layer at 0°C. The anion, $[AlCl_2Me_2]^-$, imparts air-sensitivity to the compound.[6]

The final fractional coordinates are given in Table I. Tables of bond lengths and angles, thermal parameters, and structure factors are available from the Editor upon request.

## RESULTS AND DISCUSSION

The structure of the cation is shown in Figure 1. The Yb atom is rather symmetrically bonded to the crown; the Yb- distances range from 2.23(2) to 2.32(2) Å and the Yb atom lies 0.20 Å out of the plane of the crown oxygen atoms. Thus, the 15-crown-5 molecule provides a rather snug fit for the $Yb^{3+}$ ion.[7] The two independent Yb–Cl lengths are identical within experimental error at 2.530(6)Å[8] and the Cl–Yb–Cl angle is 178.4(3)°.

Bünzli[9] has recently tabulated the 54 structures carried out on lanthanide complexes of synthetic macrocycles. The lowest coordination number found for any was 8, and the expected value for $Yb^{3+}$ is 9. We have recently showed that 15-crown-5 has the ability to cause $Al^{3+}$ to expand its coordination number to 7.[10] The title compound shows that a reduction in coordination number may also be achieved by the use of this macrocycle.

Reactions aimed at replacing the chloride while leaving the crown in place (bonded to the ytterbium) have so far been unsuccessful. Addition of TlCp to the liquid clathrate based on $[YbCl_2\cdot 15\text{-crown-}5]^+$ has allowed isolation of a salt related to $Tl[Cp_2YbCl_2]$.[11] Studies of the reactivity of the title cation are continuing.

## ACKNOWLEDGEMENTS

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2. J.-C.G. Bünzli, *Coord. Chem. Rev.*, **60**, 191 (1984).
3. Crystals of the title compound belong to the orthorhombic space group *Pnma*; cell constants $a = 11.313(7)$, $b = 10.907(5)$, $c = 17.716(7)$ A, with four formula units per unit cell and $D_c = 1.81$ g cm$^{-3}$. Least-squares refinement based on 1502 observed reflections led to a final conventional $R = 0.048$ ($R_w = 0.054$). The details of data collection and refinement are as given in 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). Anisotropic thermal parameters were used for all atoms. Hydrogen atoms of the crown ether were positioned according to geometry and were allowed to ride on the bonded carbon. The hydrogen atoms of the methyl group were located on a difference Fourier map and were likewise allowed to ride on the carbon atom. Supplementary data consisting of tables of hydrogen atom coordinates, thermal parameters for all atoms, complete bond lengths and angles, and structure factors are available from the Editor.
4. J.L. Atwood in "Inclusion Compounds", Vol. 1, Eds., J.L. Atwood, J.E.D. Davies and D.D. MacNicol, Academic Press, London (1984), pp. 375–405.
5. This material apparently consisted of alkylated Yb compounds, as well as reduced Yb species.
6. Anions ranging from $[AlMe_4]^-$ to $[AlCl_4]^-$ were probably present in solution. The ion $[AlCl_2Me_2]^-$ formed the least soluble species when paired with the cation.
7. Even with the displacement of the Yb out of the plane of the crown, the Yb–O lengths of 2.23(1), 2.25(1) and 2.31(1)Å must be regarded as short. In a typical 10-coordinate complex such as $Cp_3Y\cdot THF$, the Y–O distance is 2.451(4)Å, a difference far greater than the 0.03 Å change in ionic radii; R.D. Rogers, J.L. Atwood, A. Emad, D.J. Sikora and M.D. Rausch, *J. Organometal. Chem.*, **216**, 383 (1981).

8. The Yb-Cl distance is significantly longer than that found in the four-coordinate anion $[YbCl(CH(SiMe_3)_2)_3]$, 2.486(6) ; J.L. Atwood, W.E. Hunter, R.D. Rogers, J. Holton, J. McMeeking, R. Pearce and M.F. Lappert, *Chem. Comm.*, 140 (1978). This may be attributed to the difference in coordination number of Yb in the two compounds.

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