265 and 240 nm (ε ca. 13 000) are in agreement with the proposed structure with an extended conjugated system but limited π overlap over the folded double bond.

Acknowledgment. Financial support from the Swedish Natural Science Research Council and from the Knut and Alice Wallenberg Foundation is gratefully acknowledged.

X-ray Structures of Threaded Et_2Mg(18-crown-6) and Et_2Zn(18-crown-6)

Anthony D. Pajerski, Gretchen L. BergStresser, Masood Parvez, and Herman G. Richey, Jr.*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received January 25, 1988

Interaction of organomagnesium compounds with cryptands or crown ethers is of particular interest because disproportionation, for example as in eq 1, is often significant.[1-5] While studying

$$2R_2Mg + C \rightleftarrows RMgC^+ + R_3Mg^- \quad (1)$$

such equilibria, we obtained NMR spectra of solutions containing Tol_2Mg(15-crown-5) (Tol = *p*-methylphenyl) and Tol_2Mg(18-crown-6) species.[4] On the basis of several pieces of evidence, it was suggested that these have "threaded" structures, in which crown ether O's surround Mg in an equatorial fashion and organic groups occupy apical positions. More limited evidence indicated that Np_2Mg(15-crown-5) (Np = neopentyl) is a significant component in solutions of Np_2Mg and 15-crown-5, and it was suggested that it also may have a threaded structure.[5] This communication reports the isolation and X-ray diffraction study of solids that prove to consist of threaded Et_2Mg(18-crown-6) and Et_2Zn(18-crown-6) units.

Addition of solid Et_2Mg (1 mmol) to a stirred solution of 18-crown-6 (1 mmol) in toluene (1 mL) led to formation of a microcrystalline slurry. Heating this slurry to 70 °C and then letting it cool slowly to ambient temperature resulted in formation of long rectangular crystals, mp 114 °C.[6]

An ORTEP drawing of the structure determined for the Et_2Mg(18-crown-6) units in a crystal is shown in Figure 1.[7-9] The structure is centrosymmetric with Mg lying on the inversion center; the Mg-C bonds are perpendicular to the plane of the O's. The Mg-C bond length of 2.104 (2) Å is unusually short,[10,11] even

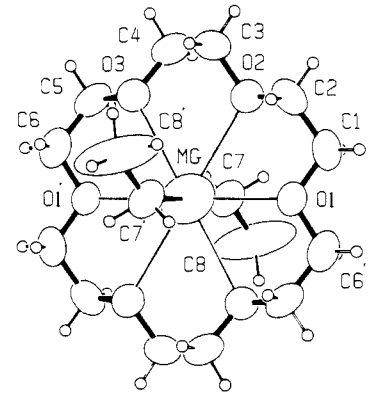


Figure 1. ORTEP drawing of Et_2Mg(18-crown-6). Atoms are shown with 50% probability ellipsoids.

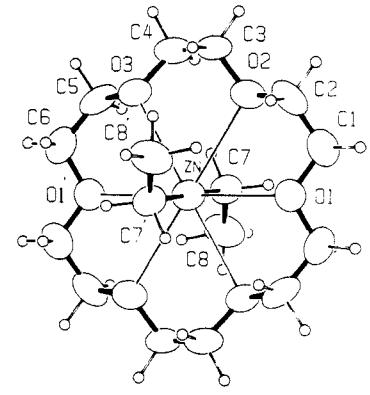


Figure 2. ORTEP drawing of Et_2Zn(18-crown-6). Atoms are shown with 50% probability ellipsoids.

shorter than that of 2.126 (6) Å in gaseous, monomeric Np_2Mg, which also has a C-Mg-C angle of 180°.[12] The Mg-O distances of 2.767 (1), 2.792 (1), and 2.778 (1) Å are nearly equal but extremely long.[13] Although significantly shorter than expected for van der Waals contact, the Mg-O distances may be unique. By using the Cambridge Crystallographic Database,[11] a search for Mg-O distances up to 3.20 Å revealed none longer than 2.58 Å. As an extreme, Et_2Mg(18-crown-6) might be regarded as almost a clathrate, having a linear Et_2Mg encapsulated within a crown ether but bonded only weakly to its oxygens.

The similar Mg-O distances in Et_2Mg(18-crown-6) contrast to the varied Mg-O distances that Bickelhaupt and his co-workers found in Ph_2Mg(1,3-xylyl-18-crown-5), in which the crown ether also has an 18-membered ring.[14] Although the O's surround the Mg in a quasi-equatorial plane, two Mg-O distances are approximately 2.21 Å, two are about 2.52 Å, and one is 4.04 Å. The similar Mg-O bond distances in Et_2Mg(18-crown-6) also contrast to the metal-oxygen distances reported recently for Me_2Al(18-

(1) Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672.
(2) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432.
(3) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *Organometallics* **1985**, *4*, 1154 (1985).
(4) Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510.
(5) Pajerski, A. D.; Parvez, M.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2660.
(6) The crystals dissolve sufficiently in benzene at 70 °C to permit taking a ^1H NMR spectrum, which shows an ethyl group to crown ether ratio of somewhat less than 2 and some evidence of decomposition.
(7) Intensity data were measured on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromatized Mo Kα radiation, the $\omega/2\theta$ scan technique, and variable scan speed. The structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations.
(8) Et_2Mg(18-crown-6), $C_{16}H_{34}O_6Mg$: monoclinic, space group $C2/c$; a = 16.267 (3) Å, b = 8.021 (4) Å, c = 15.516 (5) Å, β = 93.7 (2)°; V = 2020 (2) Å^3, Z = 4, D_{calcd} = 1.14 g cm^{-3}; R = 0.081 and R_w = 0.061 for 1047 reflections with $I > 3\sigma(I)$ (1861 unique reflections measured).
(9) The systematic absences indicated either the $C2/c$ or Cc space groups, but the E statistics were more in accord with the former. At the suggestion of a referee, however, the structure was also determined assuming the Cc space group (R = 0.084 and R_w = 0.068). Although somewhat less symmetrical, the structure does not differ drastically from that obtained assuming the $C2/c$ space group; the Mg-O distances are in the range 2.68-2.85 Å.
(10) The shortest Mg-C distance found in a search of the Cambridge Crystallographic Database (ref 11) was 2.094 (11) Å (Spek, A. L.; Voorbergen, P.; Schat, G.; Blomberg, C.; Bickelhaupt, F. *J. Organomet. Chem.* **1974**, *77*, 147).
(11) Cambridge Crystallographic Database, Crystallographic Data Centre, University Chemical Laboratory, Cambridge, England, 1987.
(12) Ashby, E. C.; Fernholt, L.; Haaland, A.; Seip, R.; Smith, R. S. *Acta Chem. Scand., Ser. A* **1980**, *34*, 213.
(13) As evident in Figure 1, the thermal parameters indicate considerable thermal motion for the Mg. We think it more likely that the Mg indeed has considerable thermal motion than that it is significantly disordered (occupying two or more positions in each of which it is considerably closer to some O's than to others). If Mg occupied more than one position, then the CH_2 group and perhaps the crown ether O's also might exhibit large thermal parameters. These parameters, however, are not particularly large in either of the relatively similar structures determined in the $C2/c$ or Cc space groups (ref 8 and 9). The structure of the Zn metallomer, in which Zn does not have particularly large thermal motions, indicates that essentially equal metal-oxygen distances to the six O's of 18-crown-6 are possible for an atom similar in size to Mg.
(14) Markies, P. R.; Nomoto, T.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.*, the following paper in this issue.

0002-7863/88/1510-4844$01.50/0

crown-6)$^+$,[15] an isoelectronic species, and for $MgCl_2$(18-crown-6).[16] The O's in the cation surround Al in an equatorial fashion, but distances range from 1.93 to 3.80 Å. In the $MgCl_2$ species, five O's lie approximately in a plane around the Mg at distances of 2.22–2.33 Å, but the sixth O is far out of that plane and beyond bonding distance. In $AlCl_2$(benzo-15-crown-5)$^+$[17] and Mg(NCS)$_2$(benzo-15-crown-5),[18] with a smaller though unsymmetrical crown ether, the Al–O (2.03–2.30 Å) and Mg–O distances (2.17–2.20 Å) are considerably shorter and more nearly equal.

Addition of hexane solutions of Et_2Zn to benzene solutions of 18-crown-6 led to slow formation of precipitates. Dissolving a precipitate in CH_2Cl_2–benzene and layering hexane over the solution resulted in slow formation of plate-shaped crystals.[19]

An ORTEP drawing of the structure determined for the Et_2Zn(18-crown-6) units in a crystal is shown in Figure 2.[20] The general geometrical features are identical with those of the Mg metallomer, but the metal–oxygen distances of 2.837 (3), 2.890 (3), and 2.873 (3) Å are even longer, and the metal–carbon distance of 1.957 (5) Å is considerably shorter. The Zn–C distance is essentially identical with that of 1.950 (2) Å in gaseous Et_2Zn, in which the C–Zn–C angle also is 180°.[21] By using the Cambridge Crystallographic Database,[11] a search for Zn–O distances up to 3.20 Å found none longer than 2.71 Å.

^{1}H NMR observations of solutions of $(Tol)_2Zn$ and 18-crown-6 indicate the presence, among other components, of a Tol_2Zn-(18-crown-6) species that probably has a threaded structure.[22] Particularly for diorganomagnesium and diorganozinc compounds with alkyl groups, however, establishing conclusively when threaded species exist in solution has been complicated by several problems, including the presence of several species in solution, equilibria that are rapid on the NMR time scale, separation of second liquid phases, and formation of solids.[22,23] We hope to report on this subject later.

The work of Bickelhaupt and his co-workers[14] and this work demonstrate the existence in solids of diorganomagnesium– and diorganozinc–crown ether species with threaded or rotaxane structures. The differences between the structures of Zn and Mg metallomers reflect the much greater propensity of organomagnesium compounds to form bonds to neutral O's.

Acknowledgment. We thank Professor Friedrich Bickelhaupt for graciously delaying publication of his work (adjoining communication) so that this communication could appear simultaneously. We also thank a referee for helpful and critical comments and suggestions. We are indebted to the National Science Foundation for support of this research.

Registry No. Et_2Mg(18-crown-6), 114692-56-7; Et_2Zn(18-crown-6), 114692-57-8; Et_2Mg, 557-18-6; Et_2Zn, 557-20-0.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for both structures (7 pages); tables of observed and calculated structure factor amplitudes for both structures (19 pages). Ordering information is given on any current masthead page.

(15) Bott, S. G.; Alvanipour, A.; Morley, S. D.; Atwood, D. A.; Means, C. M.; Coleman, A. W.; Atwood, J. L. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 485.

(16) Strel'tsova, N. R.; Ivakina, L. V.; Storozhenko, P. A.; Bulychev, B. M.; Bel'skii, V. K. *Sov. Phys. Dokl. (Engl. Transl.)* **1986**, *31*, 943.

(17) Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1796.

(18) Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1418.

(19) Their ^{1}H NMR spectrum (benzene) shows an ethyl group to crown ether ratio of 2.

(20) Et_2Zn(18-crown-6), $C_{16}H_{34}O_6Zn$: triclinic, space group $P\bar{1}$; a = 8.503 (6) Å, b = 8.719 (8) Å, c = 8.296 (7) Å, α = 111.8 (1)°, β = 114.8 (1)°, γ = 97.9 (1)°; V = 486 (2) Å^3, Z = 1, D_{calcd} = 1.33 g cm^{-3}; R = 0.056 and R_w = 0.062 for 792 reflections with $I > 3\sigma(I)$ (1820 unique reflections measured).

(21) Almenningen, A.; Helgaker, T. U.; Haaland, A.; Samdal, S. *Acta Chem. Scand., Ser. A* **1982**, *36*, 159.

(22) Fabicon, R. M. The Pennsylvania State University, unpublished results.

(23) BergStresser, G. L.; Pajerski, A. D. The Pennsylvania State University, unpublished results.

X-ray Structure of (1,3-Xylyl-18-crown-5)diphenylmagnesium: An Organometallic Rotaxane

Peter R. Markies, Tateo Nomoto, Otto S. Akkerman, and Friedrich Bickelhaupt*

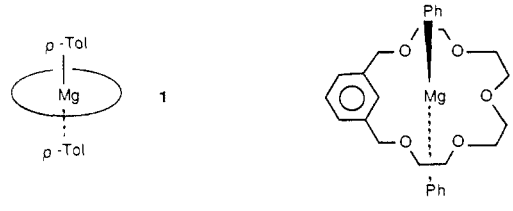
Scheikundig Laboratorium, Vrije Universiteit De Boelelaan 1083, NL-1081 HV Amsterdam The Netherlands

Wilberth J. J. Smeets and Anthony L. Spek

Vakgroep Algemene Chemie, Afdeling Kristal- en Structuurchemie, University of Utrecht Padualaan 8, NL-3584 CH Utrecht, The Netherlands

Received December 10, 1987

Crown ethers and related compounds play an increasingly important role in many areas of chemistry. Their application in main group organometallic chemistry has so far received less attention.[1,2] An interesting example is the complexation of di-*p*-tolylmagnesium with 18-crown-6 and 15-crown-5, for which Richey and Kushlan observed equivalence of the ligand protons in the ^{1}H NMR spectrum in C_6D_6 solution; they concluded that the 1:1 complex has the "threaded" structure **1**.[1d] We wish to present the X-ray crystal structure of the related crown ether complex **2** which indeed reveals such a "threaded" or rotaxane[3] structure.



In the course of our investigations of *intra*molecular coordination in organomagnesium compounds,[4,5] we required **2** as an *inter*molecular analogue for comparison purposes. When solid 1,3-xylyl-18-crown-5 (**3**)[6] was added to the solution of diphenylmagnesium in diethyl ether, a white precipitate of **2** was obtained. Crystals of **2** were grown by gradually cooling a saturated solution of **2** in toluene to −20 °C.[7] The most conspicuous aspect of the

(1) (a) Richey, H. G., Jr.; King, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 4672, and references cited. (b) Squiller, E. P.; Whittle, R. R.; Richey, H. G., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 432. (c) Squiller, E. P.; Whittle, R. R.; Richey, H. G.; Jr. *Organometallics* **1985**, *4*, 1154. (d) Richey, H. G., Jr.; Kushlan, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2510.

(2) Bott, S. G.; Alvanipour, A.; Morley, S. D.; Atwood, D. A.; Means, C. M.; Coleman, A. W.; Atwood, J. L. *Angew. Chem.* **1987**, *99*, 476. This paper gives references to other rotaxane complexes which, however, do not involve a main group organometallic compound.

(3) Schill, G. *Catenanes, Rotaxanes and Knots*; Academic Press, New York, 1971.

(4) (a) Blomberg, C.; Schat, G.; Grootveld, H. H.; Vreugdenhil, A. D.; Bickelhaupt, F. *Liebigs Ann. Chem.* **1972**, *763*, 148. (b) Freijee, F. J. M.; Van der Wal, G.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1982**, *240*, 229. (c) Villena, A. Thesis Vrije Universiteit, 1986.

(5) Markies, P. R.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.*, in press.

(6) Gray, R. T.; Reinhoudt, D. N.; Smit, C. J.; Veenstra, I. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 258.

(7) Crystal data for **2** ($C_{28}H_{34}O_5Mg$): monoclinic, space group $P2_1/n$, with a = 10.277 (2) Å, b = 13.837 (1) Å, c = 18.242 (3) Å, β = 93.89 (1)°, V = 2587.8 (7) Å^3, Z = 4, D_c = 1.219 g cm^{-3}, $F(000)$ = 1016, μ(Cu Kα) = 8.5 cm^{-1}, 4943 reflections with 3.2° < θ < 70.0° were collected on an Enraf-Nonius CAD4F diffractometer with Ni filtered Cu Kα radiation (λ = 1.54184 Å). The structure was solved by direct methods (SHELXS86) and difference Fourier techniques and refined by full-matrix least-squares (SHELX76) to an R value of 0.054 R_w = 0.059, $w^{-1} = \sigma^2(F)$ for 1979 reflections with $I > 2.5\sigma(I)$. In the final stages of the refinement, hydrogen atoms were introduced on calculated positions; all non-hydrogen atoms were refined with anisotropic thermal parameters.

0002-7863/88/1510-4845$01.50/0