

Pedersen C J. Cyclic polyethers and their complexes with metal salts.

J. Amer. Chem. Soc. 89:7017-36, 1967.

[Elastomer Chemicals Dept., E.I. du Pont de Nemours and Co., Wilmington, DE]

The discovery of the first crown ether is described. Forty-seven other aromatic and saturated polyethers were synthesized and their properties determined. Many form stable crystalline complexes with alkali and alkaline earth salts. Some saturated crown ethers solubilize potassium hydroxide and permanganate in aromatic hydrocarbons. [The SC¹® indicates that this paper has been cited in over 1,165 publications since 1967.]

Charles J. Pedersen
57 Market Street
Salem, NJ 08079

March 20, 1985

The first cyclic polyether synthesized was called the *crown* because of the appearance of its molecular model and its ability to crown cations. The cyclic polyethers as a class were called the *crown compounds*. This commentary summarizes how I discovered the crown ethers and the conditions under which their varied developments were initiated.¹ Reasons for the frequent citation of the resulting paper are offered.

In 1961, at age 57, I began to study the effects of uni- and multidentate phenolic ligands on the catalytic properties of the VO group. The desired ligands, up to and including the quadridentate, had been synthesized. Now, the quinquevalent ligand, bis(2-(*o*-hydroxyphenoxy)ethyl) ether, was to be prepared by reacting a catechol derivative containing a protected hydroxyl (contaminated with 10 percent catechol) with bis(2-chloroethyl) ether. The expected quinquevalent ligand was obtained, but nature lent a hand to provide the hexadentate dibenzo-18-crown-6 in 0.4 percent yield. This is the extent of serendipity. The by-product was slightly soluble in methanol, contained no hydroxyl, and was solubilized by any soluble sodium compound. The compound was forming stable sodium complexes, a feat not previously achieved by any synthetic compound. Other crown ethers were synthesized, and when their unique properties had

been determined, an exhilarating period of research was inaugurated: every successful experiment produced a significantly novel result.

The crown ethers might have been still-born in another environment. They were discovered in the Elastomer Chemicals Department of E.I. du Pont de Nemours and Company, but what had they to do with elastomers? Moreover, the small amount of the by-product might have been tossed out or disregarded as something other than the desired product. However, with the support of the top departmental management (C.J. Harrington, A.S. Carter, H.E. Schroeder, and R. Pariser), I worked independently with these compounds for nearly eight years. During the period leading to the paper, my sole co-worker was T.T. Malinowski, a laboratory technician. I also had the resources of the analytical groups and the chance to consult with anyone on the technical staff of the company.

The editor of the *Journal of the American Chemical Society*, Gates Marshall, wrote of the manuscript: "You are clearly reporting a monumental piece of work...." But he complained that the experimental section "...looked as though it had been copied *verbatim* from a laboratory notebook." He contributed to the frequency of citation by allowing two unusual features in the paper: length (20 pages) and a new system of nomenclature (crown) for identifying compounds whose official names boggle the mind. The paper is the primary reference for the crowns, but it also contains the germs of varied later developments stemming from the original discovery. Many able investigators have founded their own systems, such as cryptates, host-guest chemistry, and the membranes and the ion-sensitive electrodes of the biochemists, who were the first to evince interest in the crown ethers.²

In 1968, I received the Delaware Section Award of the American Chemical Society.

THE CROWNING

The alkaline earth cations

And the alkali too,

Used to act like freeborn lions,

Scorning some things to do.

Organic ligands they disdained

Till crown ethers were found.

Now with these compounds science ordained

They can be meekly crowned.

1. Pedersen C J. Synthetic multidentate macrocyclic compounds. (Izatt R M & Christensen J J, eds.) *Synthetic multidentate macrocyclic compounds*. New York: Academic Press, 1978, p. 1-51. (Cited 50 times.)
2. Hrbko M. *Crown compounds: their characteristics and applications*. New York: Elsevier, 1982. 273 p.