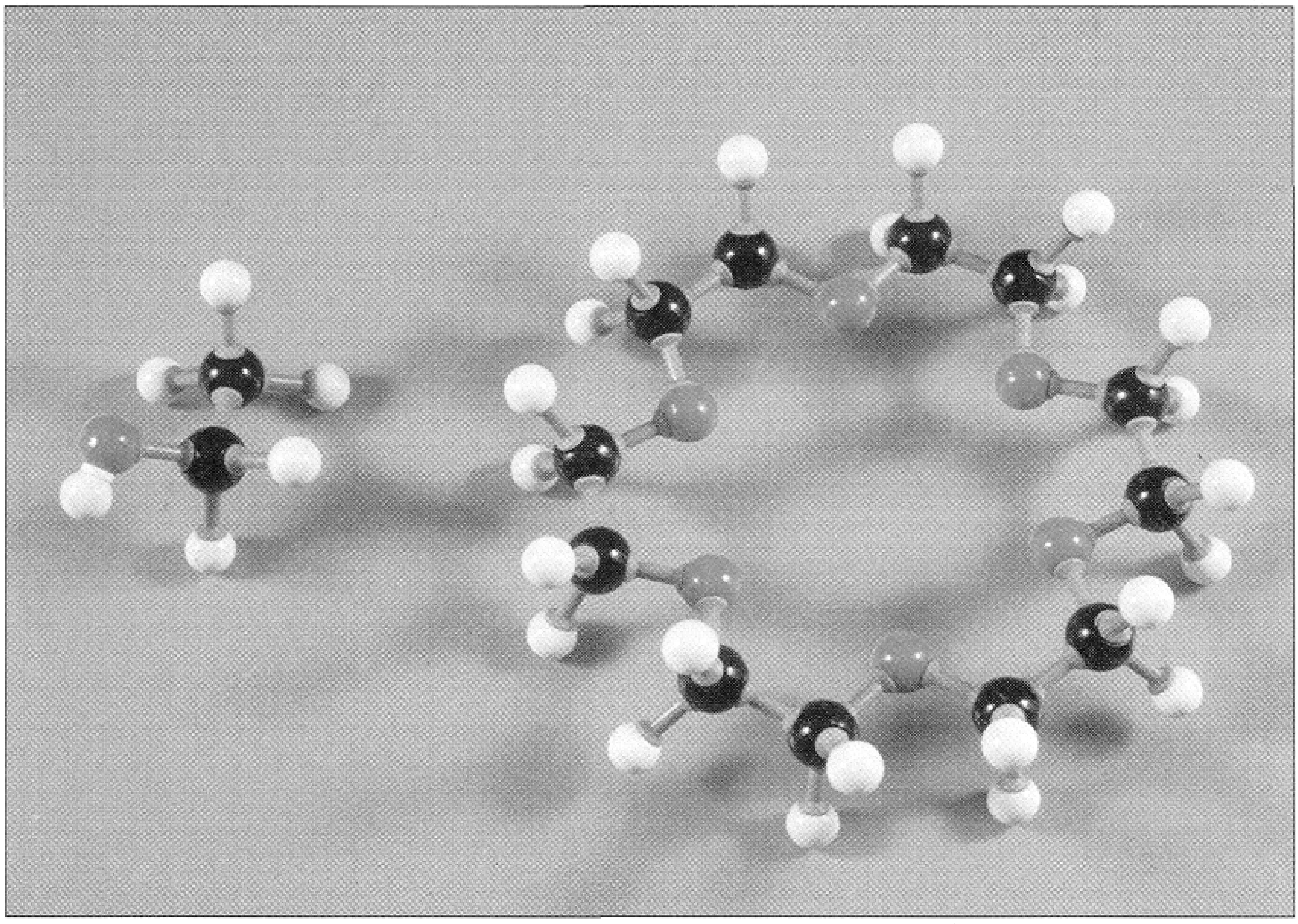

**Figure 1.** Models of 18-crown-6 (on the right) and ethyl alcohol. The black balls represent carbon atoms, the red balls oxygen atoms, and the white balls hydrogen atoms.

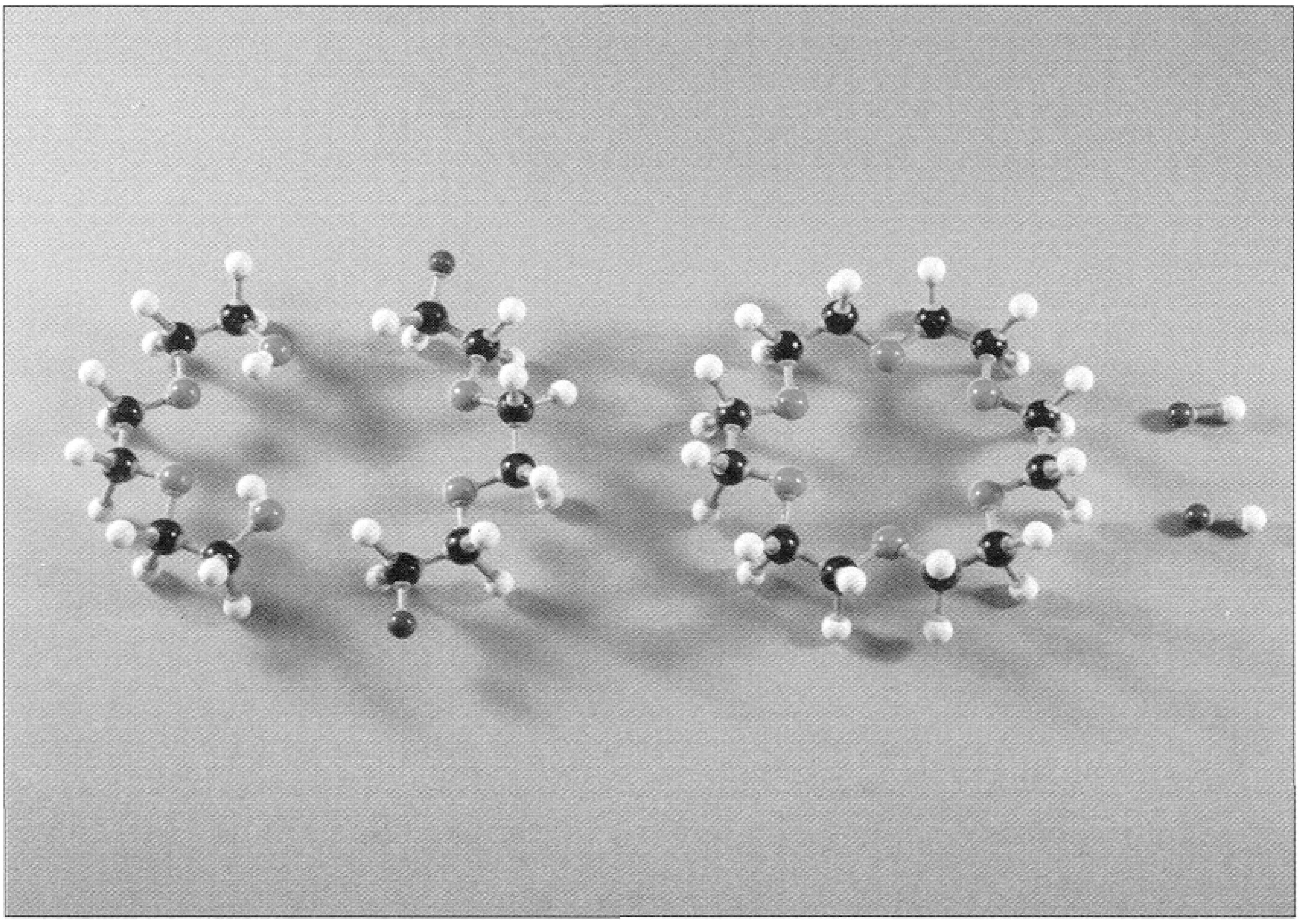

**Figure 2.** Models of the reaction of triethylene glycol (extreme left) with the dichloride (next to left) to form 18-crown-6 and two hydrochloric acid molecules.

# Crown-6 and the Future

Jerald S. Bradshaw

I want to explain why I have CROWN-6 on my license plate. Crown-6 has nothing to do with dental work; it represents the type of chemistry my research associates and I are involved in. The license plate should read 18-crown-6, but the plate will accommodate only eight characters.

A model of 18-crown-6 is shown in figure 1. The black balls in the model are carbon atoms, the red balls are oxygen atoms, and the white balls are hydrogen atoms. Notice that each carbon is bonded (connected) to two hydrogen atoms, an oxygen atom, and another carbon atom. The carbon atoms reveal that 18-crown-6 is an organic chemical compound. Organic chemistry is the chemistry of carbon compounds. People say organic chemistry is really difficult to learn, but all you need to remember is that carbon has four bonds—*every* carbon atom has four bonds. In most cases, carbon bonds to two hydrogen atoms, one oxygen atom, and another carbon atom. Sometimes carbon has two bonds or even three bonds to the same atom but always has four total bonds.

18-crown-6 is a very unusual molecule called a macrocyclic compound (refer to figure 1). It has an oxygen, two carbons, an oxygen, two carbons and so on in a repeating arrangement in the form of a large ring. That's where the term *macrocycle* comes from. *Macro* means large, *cycle* means ring. Notice that the oxygen atoms are pointing towards the center making a hole or cavity in the molecule. 18-Crown-6 is obviously more complicated than the simple compound on the left in figure 1. That two-carbon compound is ethyl, or spirit alcohol. Notice that its back carbon atom has four bonds, three

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Jerald S. Bradshaw is Professor of Chemistry at Brigham Young University, where this essay was originally presented as the Distinguished Faculty Lecture for 1992. Professor Bradshaw writes: "Special thanks to my wife, Karen, for thirty-eight years of love, support, and listening to many of my lectures both here and abroad; to more than one hundred students and research associates for their research efforts through twenty-six years; and to colleagues Reed Izatt, the late James Christensen, Kent Dalley, and John Lamb for years of exciting research."

to hydrogen atoms and one to the front carbon atom. The front carbon has a bond to oxygen, two to hydrogens, and the fourth to the back carbon atom. The oxygen atom is also bonded to a hydrogen atom. This carbon-oxygen-hydrogen group is typical of alcohols.

Charles Pedersen, a chemist at duPont, discovered 18-crown-6 in about 1964.[1] I want to show you how he prepared this compound. An important aspect of organic chemistry is that we can convert one organic compound or a group of organic compounds into a new organic compound. Figure 2 shows Pedersen's reaction for forming 18-crown-6. The two organic compounds on the left are the reactants. The compound on the extreme left has two alcohol groups. Between these alcohol groups, we have carbon-carbon-oxygen-carbon-carbon-oxygen-carbon-carbon. This arrangement is like that in 18-crown-6. Actually, it is half of 18-crown-6. The other reactant also has the carbon-carbon-oxygen arrangement, but on the ends, instead of an alcohol, there are chlorine atoms (the green balls in the model represent chlorine). Pedersen found that when he treated these two compounds together with caustic, the alcohol oxygen atoms attacked the carbon atoms next to the chlorines displacing the chlorine atoms. New bonds form between those two carbons and the former oxygen atoms of the alcohols creating 18-crown-6. Also, the hydrogen atoms of the former alcohols and the displaced chlorine atoms get together to form hydrogen chloride (hydrochloric acid).

It's impossible in chemistry to use models to explain every reaction. There are too many reactions, and we do not have time to prepare the models. Figure 3 is the organic chemist's two-dimensional way of showing the reaction of figure 2 without using models. The point where two lines connect represents a carbon atom containing two hydrogen atoms ($CH_2$). Remember, every carbon atom has four bonds. The carbon atom at the point must be bonded to two hydrogen atoms to go with bonds to one oxygen (O) and another carbon atom. Triethylene glycol has $HO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$ in a chain. Bis(2-chloroethyl)ethane, the dichloride reactant, has the same structure except the OH groups on the ends are replaced by chlorine atoms (Cl). Now you can see by the dotted arrows that the oxygen atoms of the alcohol groups attack the carbon atoms of the dichloride displacing the chlorine atoms. Two new C-O bonds are formed (between oxygen 1 and carbon 2 and oxygen 10 and carbon 9) as are the two H-Cl molecules.

The scientific name for 18-crown-6 is 1,4,7,10,13,16-hexaoxacyclooctadecane. Now that's a mouthful. Nomenclature in organic chemistry looks difficult, but when you break it down, it is straightforward. *Hexa* is six; there are six oxygen atoms (*oxa*).

numbers tell where they are in the ring. *Octadeca* is eighteen; there are eighteen total ring (*cyclo*) members. The *ane* ending indicates that this compound is in the alkane family. Pedersen realized that the name was very complicated, so he devised a simplified way to name it. He looked at the model and thought it looked like a crown. And so, rather than using the long complicated name, he called it a crown compound. If you count from oxygen number one (see figure 3) all the way around to the last carbon atom, number eighteen, you count eighteen atoms in the ring. There are six oxygen atoms. Thus, he named this compound 18-crown-6.[2]

When Pedersen made 18-crown-6, he also made 15-crown-5 (15 ring members, 5 oxygen atoms), and many, many more crown compounds. If he had only made these compounds, everyone would have thought that it was interesting that the molecules were in the form of a macroring, but he never would have been given the Nobel Prize. Pedersen received the Nobel Prize for what these compounds do. 18-Crown-6 causes an inorganic salt to dissolve in an organic solvent. In the morning, when you prepare Cream of Wheat®, you put a small amount of salt in the water and it dissolves immediately. Everyone knows that sodium chloride (NaCl), common table salt, dissolves in water. But if you placed NaCl in cleaning fluid or turpentine, it would not dissolve. Pedersen discovered that if 18-crown-6 were dissolved in the cleaning fluid, NaCl and other common salts would also dissolve. Thus, 18-crown-6 causes the salt to dissolve in the cleaning fluid. This important property warrants demonstration.

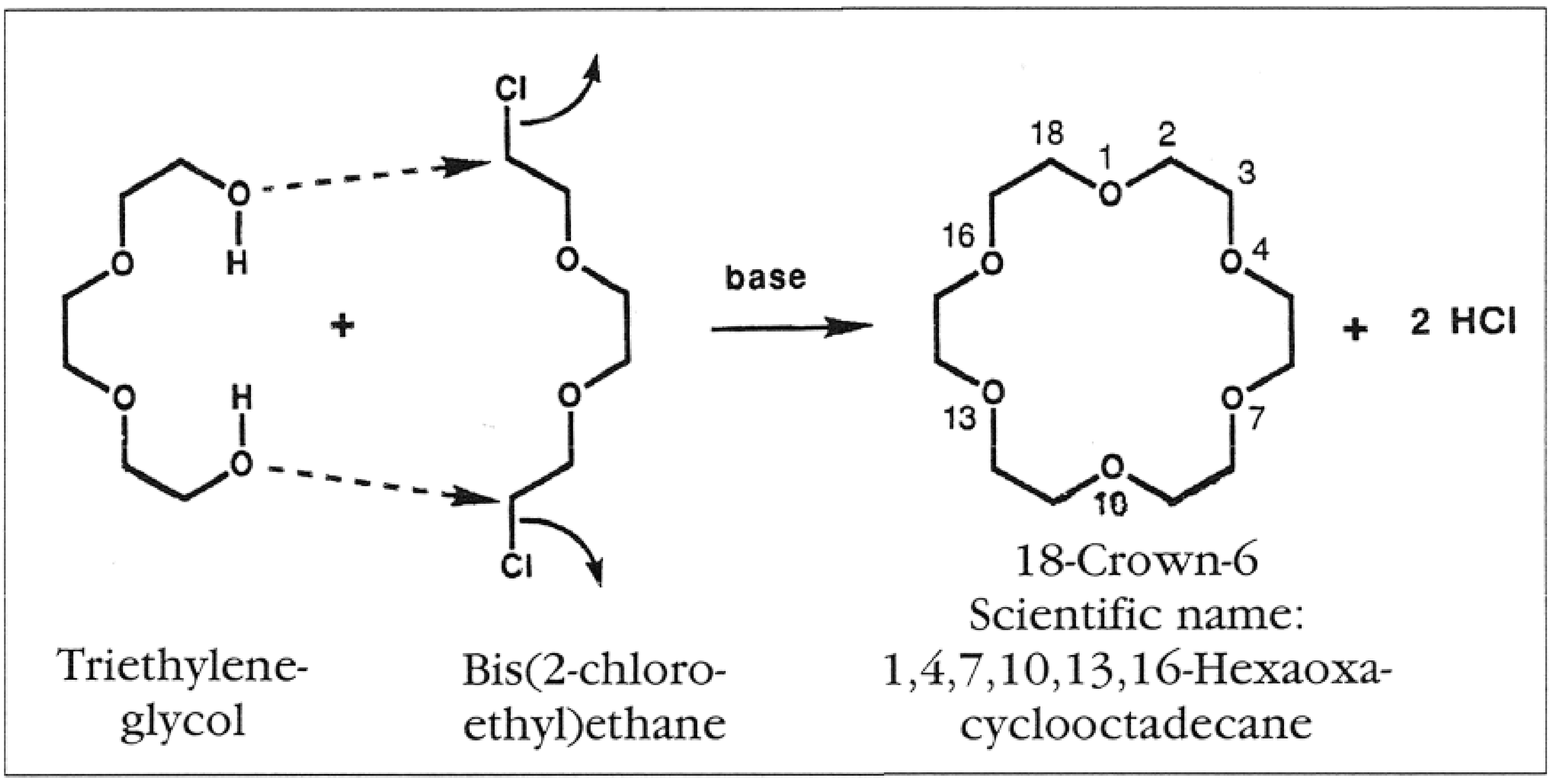
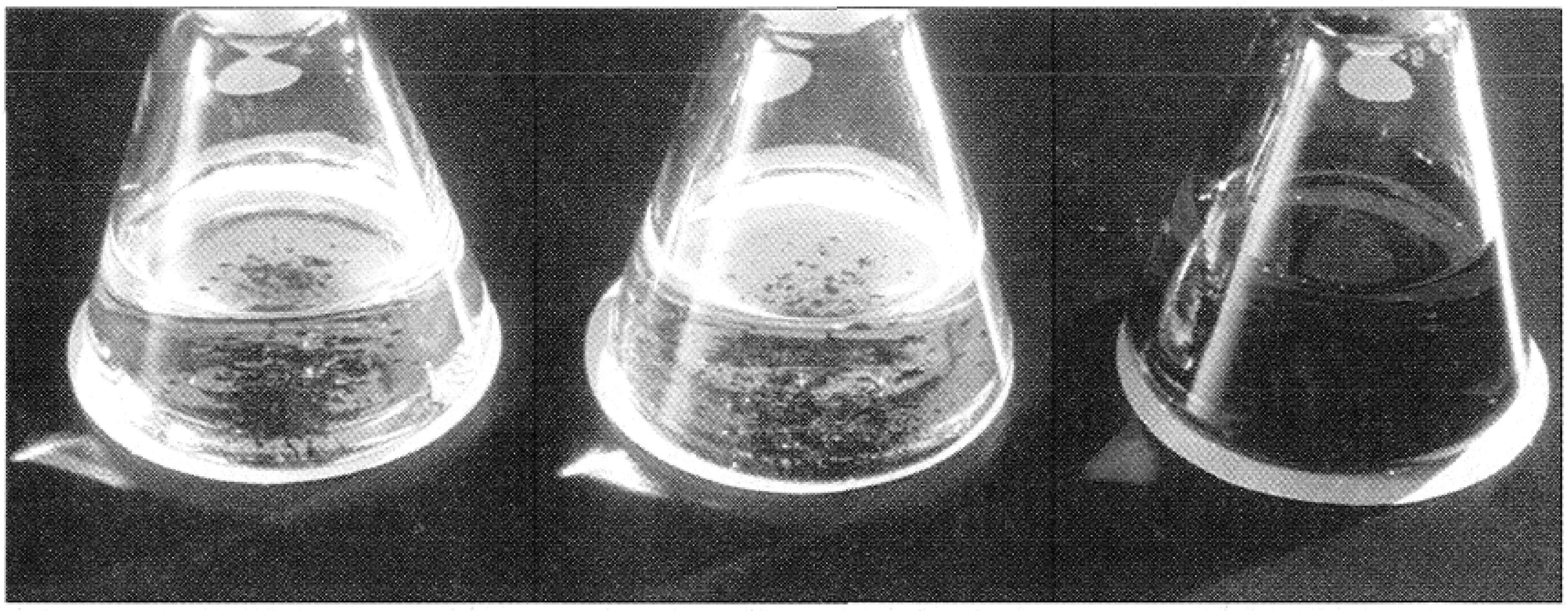


**Figure 3.** Chemist's notation for Pedersen's Nobel Prize reaction to form 18-crown-6. The angles are carbon atoms containing two hydrogen atoms ($CH_2$), H is hydrogen, O is oxygen, and Cl is chlorine.

At the top of figure 4 are three flasks containing liquids. The one on the right has water with purple salt, potassium permanganate ($KMnO_4$), dissolved in it. We could have used NaCl, but it would make a colorless solution and we could not easily see that it dissolved. The first and second flasks contain chloroform (a cleaning fluid) which does not dissolve $KMnO_4$. You can see the purple crystals in the bottom of the flask. Some 18-crown-6, which is a white solid, is added to the top left flask. Notice in the second flask in the middle of figure 4 that some light purple swirls appear as the $KMnO_4$ dissolves. The color is more noticeable in the flask on the right which has stood for a few minutes. As the 18-crown-6 dissolves and comes into contact with the purple salt, it causes the salt to dissolve and give a light purple color. If more 18-crown-6 were added, more purple salt would dissolve. The flasks at the bottom of figure 4 summarize what we have seen. Purple $KMnO_4$ dissolves instantly in water (flask on the right). The purple salt does not dissolve in chloroform (flask in the middle) unless 18-crown-6 is added to the chloroform (flask on the left). Isn't this beautiful? Who said organic chemistry was dull? This important property is why Charles Pedersen was awarded a share in the Nobel Prize in 1987.[3]

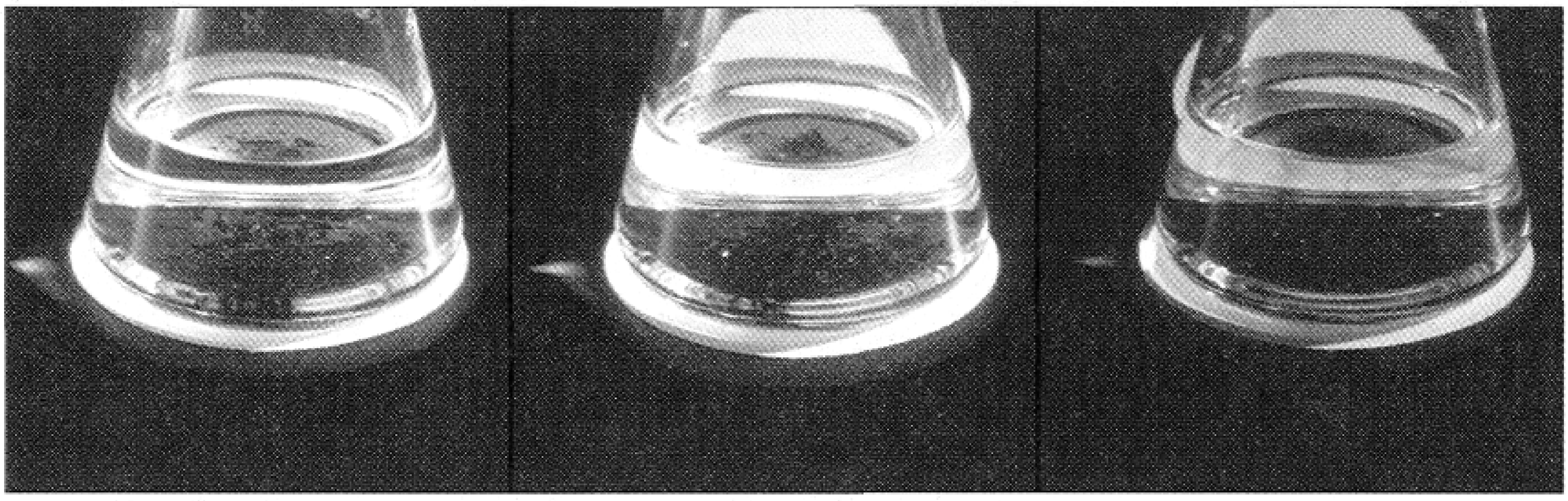
Pedersen published his first paper in 1967,[4] and many chemists everywhere were extremely interested in these new chemical compounds. Two of the interested people were Reed M. Izatt, my colleague in the Chemistry Department, and the late James J. Christensen, who was in the Chemical Engineering Department. Reed and Jim had a special technique to study the interaction of organic molecules with salts.[5] When they saw Pedersen's paper, they realized that their technique could help explain why $KMnO_4$ dissolved in an organic solvent containing 18-crown-6. Reed and Jim were among the first to visit Charles Pedersen at duPont. There he graciously gave them some 18-crown-6 for their studies. They learned early that 18-crown-6 interacted very strongly with potassium salts, not at all with lithium salts, and only weakly with cesium salts. As they thought about these results and looked at models of 18-crown-6 and models of potassium, lithium, and cesium ions, they realized that potassium ions fit exactly in the cavity of 18-crown-6, but lithium is too small and cesium too big to fit in the cavity.

This discovery is shown in figure 5 which has space-filling models of 18-crown-6 and cesium ($Cs^+$) (top dark ball), potassium ($K^+$), and lithium ($Li^+$) ions. Space-filling models show the effective space for each atom. The red oxygen atoms are pointing into the



**Chloroform**
**Potassium permanganate**
**not dissolved**

**Water**
**Potassium permanganate**
**dissolved**



**After addition of 18-C-6**

**No time**

**Short time**

**4 minutes**

**$CHCl_3$**
**Some 18-C-6**

**$CHCl_3$**
**No 18-C-6**

**Water**

**Figure 4.** Pictures of an experiment to show that 18-crown-6 (18-C-6) causes an inorganic salt ($KMnO_4$) to dissolve in chloroform ($CHCl_3$).

center of the cavity as before. You can see $K^+$ is about the right size to fit in the cavity, $Li^+$ is too small (it would fall right through) and $Cs^+$ is too large. On the bottom of figure 5, we see the 18-crown-6-$K^+$ molecule with the $K^+$ snugly inside the cavity and touching each oxygen atom. Notice that $K^+$ is now surrounded on the outside of the macrocycle by carbon and hydrogen atoms which are the major constituents of an organic compound. Thus, the cation (positively charged ion) of the salt becomes encased in the organic compound and becomes soluble in an organic solvent. This is how 18-crown-6 causes $KMnO_4$ to be soluble in chloroform.

Professors Izatt and Christensen published a paper in 1968 in *Science*[6] which caught the attention of organic and inorganic chemists everywhere. They showed that 18-crown-6, a synthetic organic molecule, recognized another molecule. There are many naturally occurring molecules that recognize other molecules, but 18-crown-6 was one of the first synthetic molecules to do this. In this case, it recognizes potassium because potassium fits in the cavity, but it won't recognize lithium because lithium falls through the crown.

I had arrived at BYU shortly before their discovery. Reed, Jim, and I sent a proposal to the National Science Foundation (NSF) to study the properties of these and similar crown macrocycles in greater detail. We received a grant from NSF, and we have had continuous funds from one of the federal or state granting agencies for over twenty years. Crown compounds could not be purchased at that time because they were so new. In our joint studies, I and my research students have prepared the needed crown compounds, and Reed and Jim and their students have studied their interactions with a variety of inorganic and organic salts. It's been a very fruitful association for all three of us. I want to show you some of the crown compounds that we have made in my laboratory.

The first series of compounds that we synthesized were crown macrocycles where sulfur atoms (S) have been substituted for oxygen atoms. In figure 6, you see Pedersen's 18-crown-6 on the left and our sulfur-containing 18-crown-6 in the middle. This specific compound has two sulfur and four oxygen atoms in the macroring, a structure which represents dozens of compounds, as I will show later. The names listed under the sulfur-containing 18-crown-6 compound are graduate students who prepared these compounds. Joseph Hui was the first student to work on crown compounds in our laboratory. He received his Ph.D. in 1974. Although Barry Haymore worked with Professor Izatt, he made a number of sulfur-containing

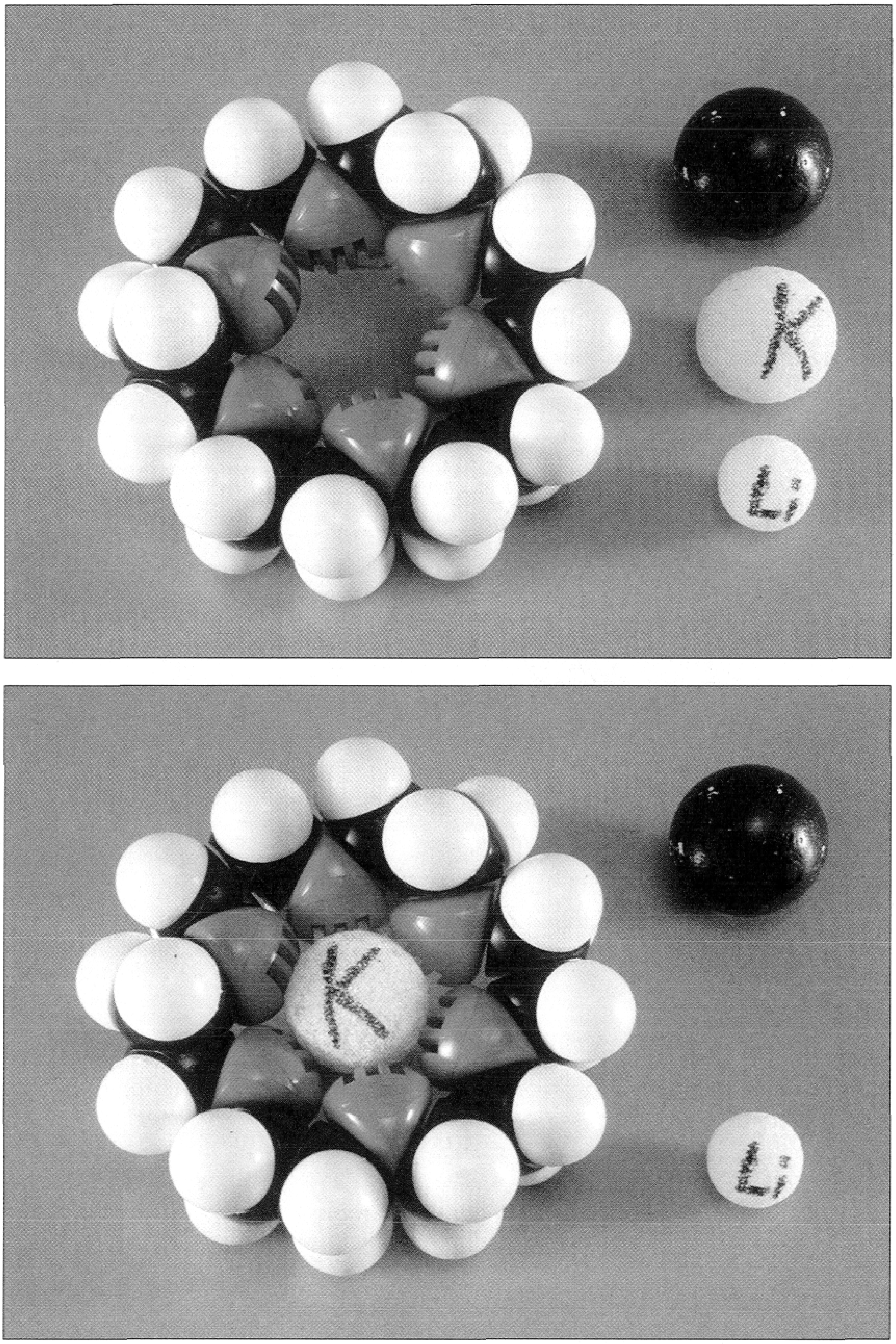
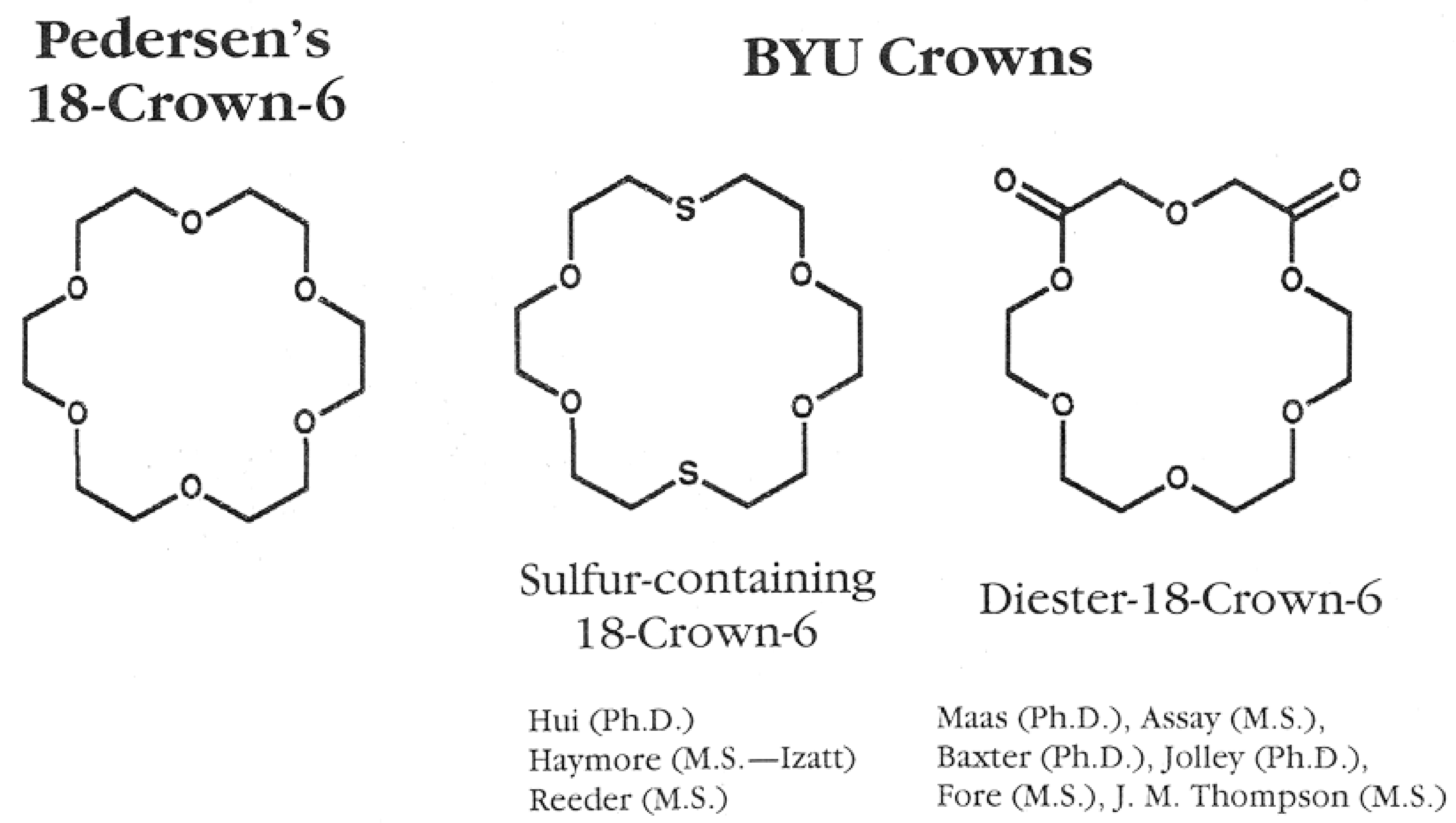


**Figure 5.** A space-filling model of 18-crown-6 and cesium (top right), potassium (K), and lithium (Li) ions (top figure). K fits snugly inside the 18-crown-6 cavity (bottom figure).

crown compounds. There were many undergraduate chemistry students that worked in our laboratory. Their names, too, appear on many of our scientific papers.

The diester-crown compounds (figure 6, on the right) were next prepared and studied under a new NSF grant. Two carbon atoms have double bonds each to an oxygen atom. The carbons still have four bonds, but only three groups are attached to those two carbon atoms. There are more graduate students who prepared these diester compounds than the sulfur-containing crowns. Many more compounds were prepared because of variations of ring size, number and positions of the carbon-oxygen bonds, and the possibility of having sulfur atoms substituted for oxygen atoms.



**Pedersen's 18-Crown-6**

**BYU Crowns**

Sulfur-containing 18-Crown-6

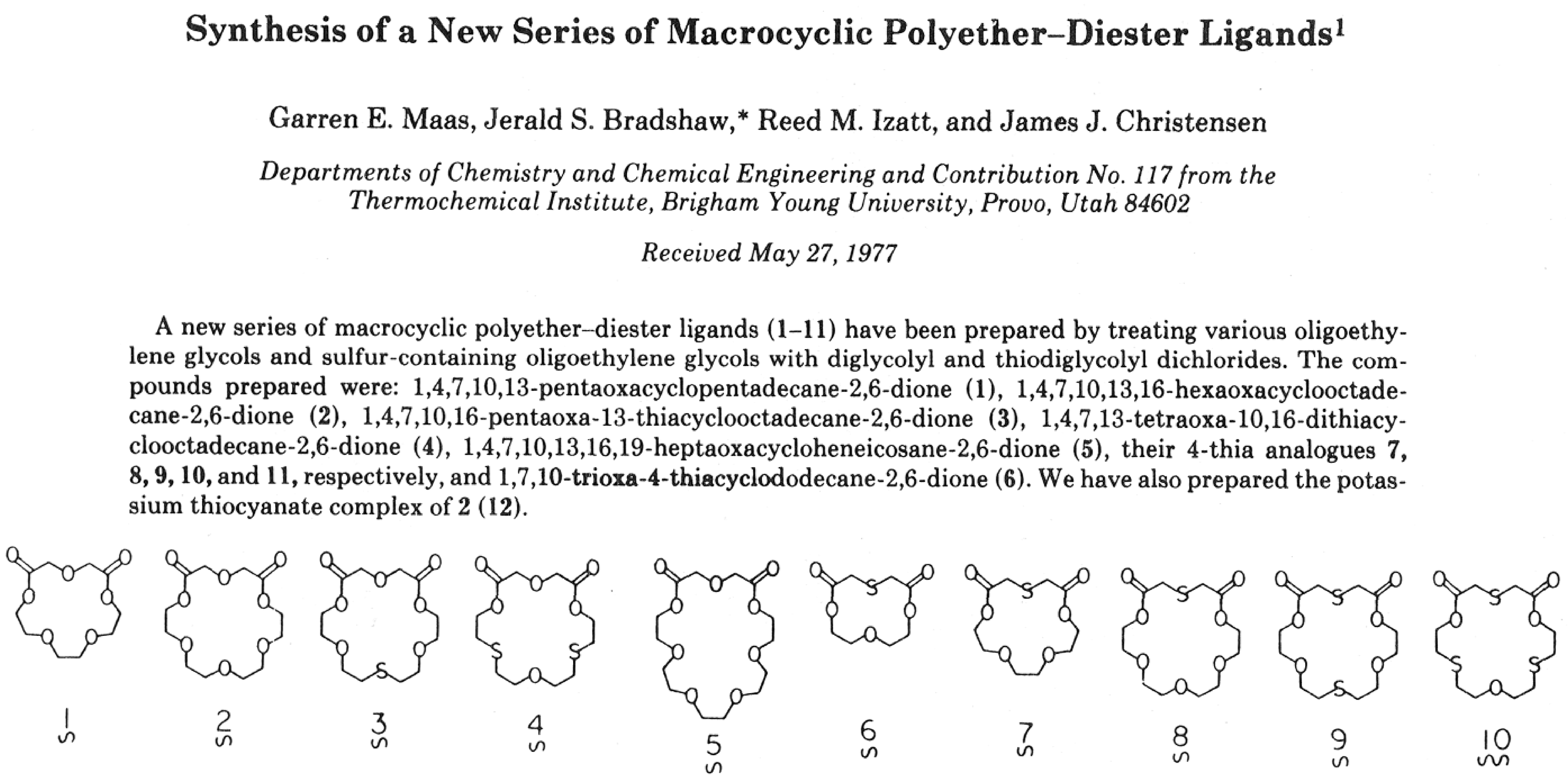
Diester-18-Crown-6

Hui (Ph.D.)
Haymore (M.S.—Izatt)
Reeder (M.S.)

Maas (Ph.D.), Assay (M.S.),
Baxter (Ph.D.), Jolley (Ph.D.),
Fore (M.S.), J. M. Thompson (M.S.)

**Figure 6.** Structures representing the sulfur-containing and diester-crown compounds prepared at BYU as compared to Pedersen's 18-crown-6. Graduate research assistants are listed.

To show the great variety of diester-crowns, I want to answer a question that people have been asking me for over twenty-five years. Here's the question: "Jerald, if you're not teaching this summer, why are you down at BYU every day?" Research is not finished unless or until it is published. We write many manuscripts every year that are published in various scientific journals. The first page of our paper on Garren Maas's work on the diester-crown macrocycles[7] is shown in figure 7. The structures of the compounds reported in this paper are also shown in the figure. You can see 12-membered to



# Synthesis of a New Series of Macrocyclic Polyether–Diester Ligands[1]

Garren E. Maas, Jerald S. Bradshaw,* Reed M. Izatt, and James J. Christensen

*Departments of Chemistry and Chemical Engineering and Contribution No. 117 from the Thermochemical Institute, Brigham Young University, Provo, Utah 84602*

*Received May 27, 1977*

A new series of macrocyclic polyether–diester ligands (**1**–**11**) have been prepared by treating various oligoethylene glycols and sulfur-containing oligoethylene glycols with diglycolyl and thiodiglycolyl dichlorides. The compounds prepared were: 1,4,7,10,13-pentaoxacyclopentadecane-2,6-dione (**1**), 1,4,7,10,13,16-hexaoxacyclooctadecane-2,6-dione (**2**), 1,4,7,10,16-pentaoxa-13-thiacyclooctadecane-2,6-dione (**3**), 1,4,7,13-tetraoxa-10,16-dithiacyclooctadecane-2,6-dione (**4**), 1,4,7,10,13,16,19-heptaoxacycloheneicosane-2,6-dione (**5**), their 4-thia analogues **7**, **8**, **9**, **10**, and **11**, respectively, and 1,7,10-**trioxa-4-thiacyclo**dodecane-2,6-dione (**6**). We have also prepared the potassium thiocyanate complex of **2** (**12**).

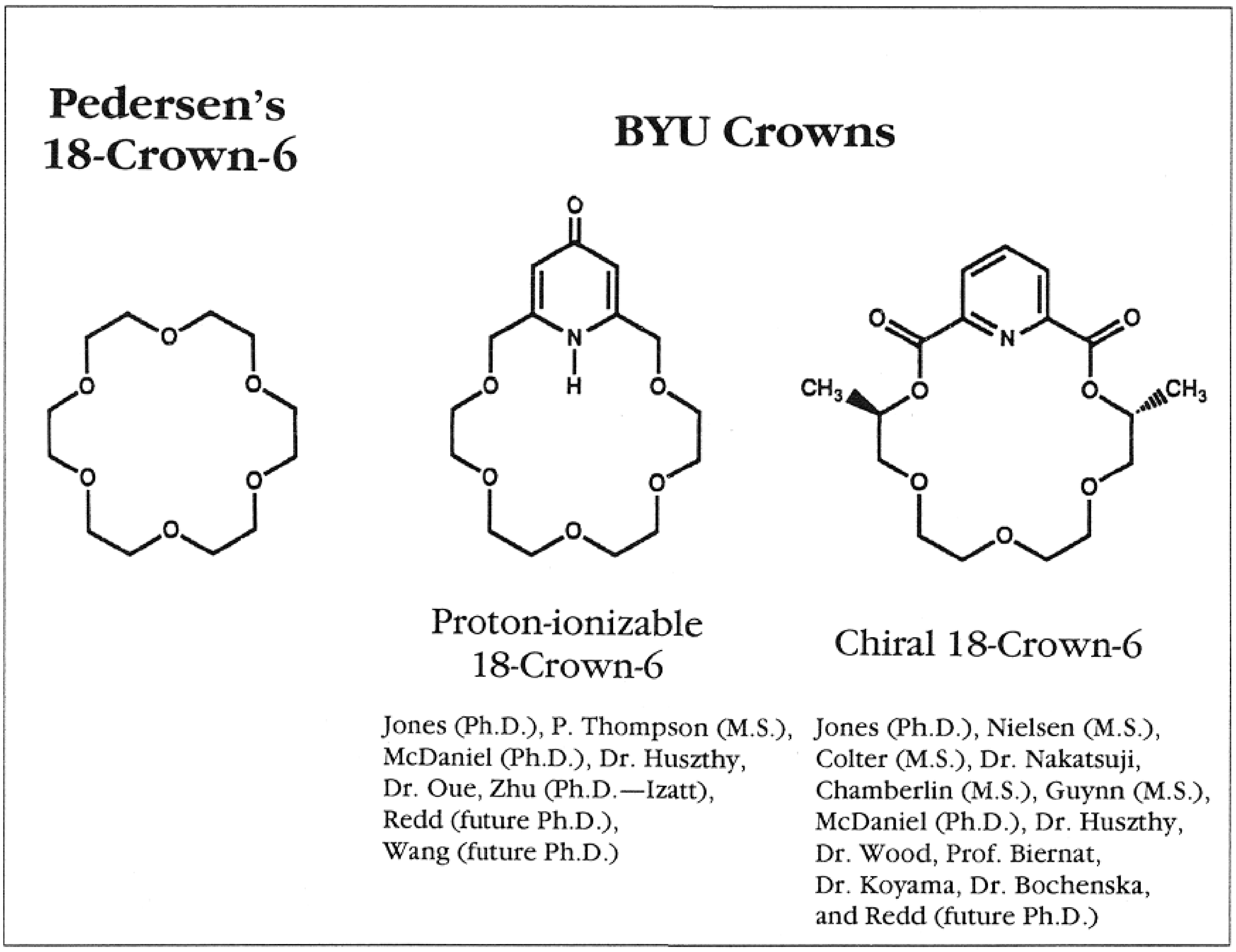
**Figure 7.** First page of our initial paper on the diester-crown compounds. See Garren E. Maas and others, *Journal of Organic Chemistry 42* (November 1977): 3937–41.

21-membered rings with sulfur atoms in various positions. Thus, each structure in figure 6 represents dozens, even hundreds of crown compounds. We always make a variety of compounds in an effort to find the right macrocycle to interact with a specific cation.

Figure 8 shows two series of crown compounds which contain small 6-membered subcyclic rings. The small ring in the macrocycle on the right is a pyridine ring. More student names are listed because of an even greater variety of macrocycles that were prepared. Dr. Yohji Nakatsuji, a postdoctoral fellow, started our group synthesizing these more complicated macrocycles.[8] Others on the list who have doctoral or professorial titles were postdoctoral fellows or visiting faculty. This work could not have been done without all of these great researchers. For example, Ty Redd is a faculty member at Southern Utah University. He has prepared some of these compounds with a second nitrogen atom in the small 6-membered ring. Dr. Peter Huszthy is making compounds with different groups coming out of the macrocycles at different angles (the structure on the right in figure 8). Tingmin Wang is currently studying the interactions of these crowns with various types of inorganic and organic salts.

The next crowns prepared in our laboratory had nitrogen atoms (N) substituted for oxygen atoms (figure 9). A nitrogen atom always has three bonds. The nitrogens in the structure in the middle of figure 9 are bonded to two carbons in the ring and to an ethyl carbon atom ($C_2H_5$). Dr. Krzysztof Krakowiak has made hundreds of these compounds, and he has devised brilliant new methods for their syntheses.[9] The last compound in figure 9 has two crown rings tied together through the nitrogen atoms. These materials have a "butterfly" shape. Dr. Haoyun An, who has recently finished his Ph.D., has made many of these latter compounds.[10] Figure 10 is the first page of a paper showing Dr. Krakowiak's method to synthesize some of the nitrogen-containing crown compounds.[11] (Daria, his wife, also works with us.) Notice the different kinds of compounds with varying ring sizes and numbers of nitrogen atoms.

We have prepared three-dimensional crown compounds. Figure 11 shows the cryptands and suitcase-shaped compounds we have prepared. The cryptands are football-shaped molecules which have a cavity that is completely encased inside the compound. Metal ions interact very strongly with the cryptands. Dr. Krakowiak has discovered new simple methods to prepare these materials.[12] Dr. An has recently prepared the suitcase-shaped molecules shown in figure 11.[13]



**Pedersen's 18-Crown-6**

**BYU Crowns**

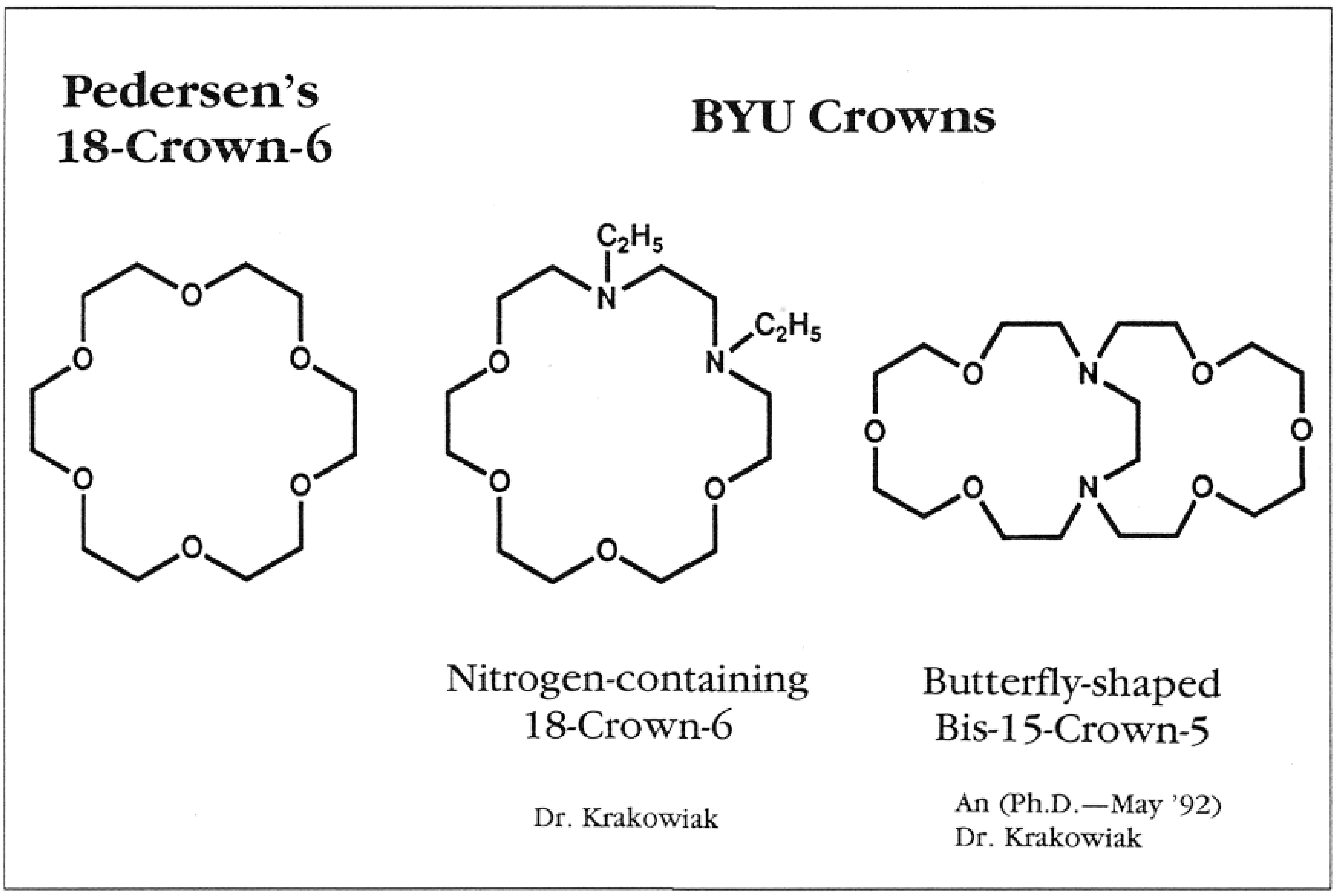
Proton-ionizable 18-Crown-6

Jones (Ph.D.), P. Thompson (M.S.), McDaniel (Ph.D.), Dr. Huszthy, Dr. Oue, Zhu (Ph.D.—Izatt), Redd (future Ph.D.), Wang (future Ph.D.)

Chiral 18-Crown-6

Jones (Ph.D.), Nielsen (M.S.), Colter (M.S.), Dr. Nakatsuji, Chamberlin (M.S.), Guynn (M.S.), McDaniel (Ph.D.), Dr. Huszthy, Dr. Wood, Prof. Biernat, Dr. Koyama, Dr. Bochenska, and Redd (future Ph.D.)

**Figure 8.** Structures representing crown compounds containing additional small rings (the small ring on the right is a pyridine) and chiral positions.



**Pedersen's 18-Crown-6**

**BYU Crowns**

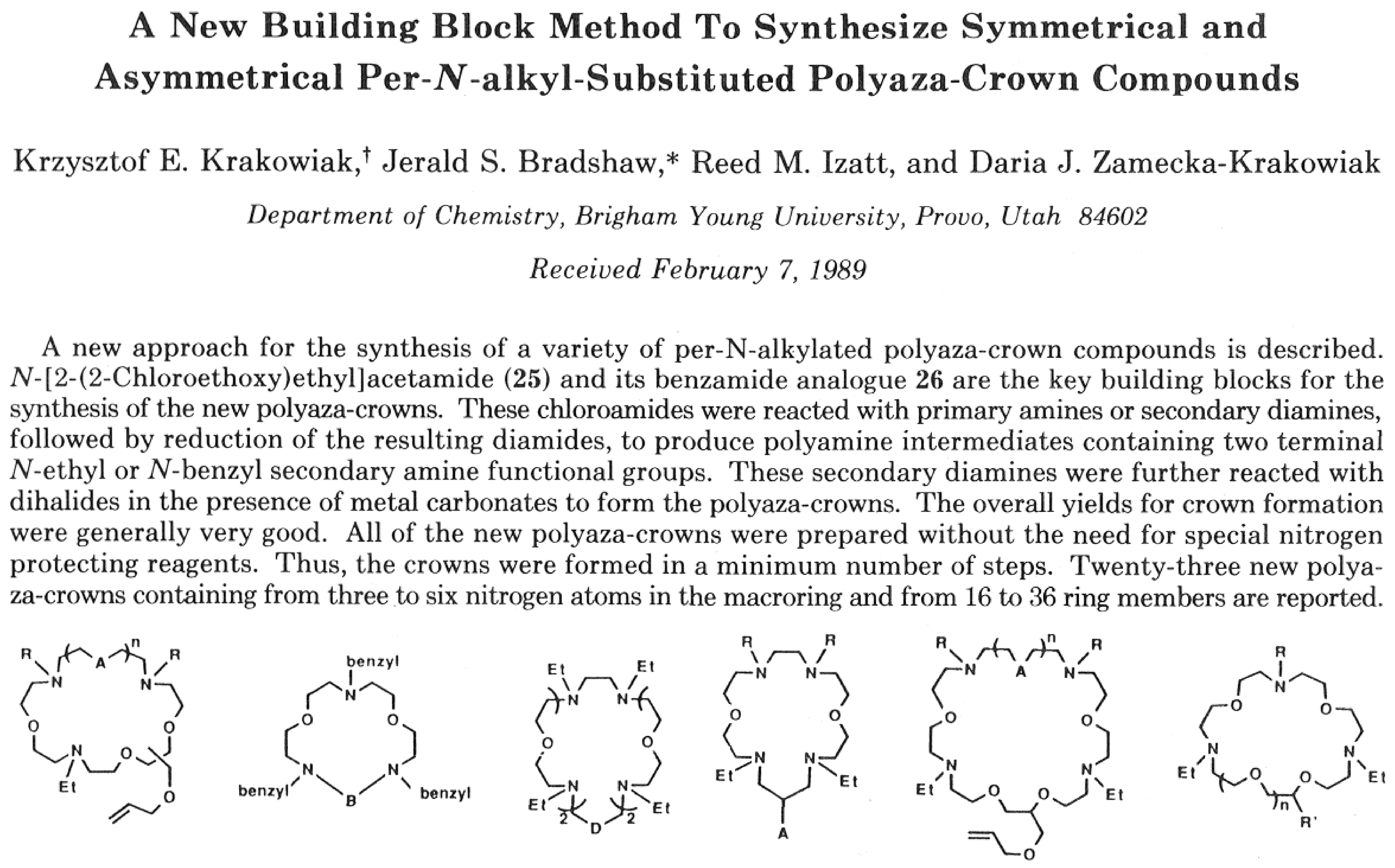
Nitrogen-containing 18-Crown-6

Dr. Krakowiak

Butterfly-shaped Bis-15-Crown-5

An (Ph.D.—May '92)
Dr. Krakowiak

**Figure 9.** Structures representing nitrogen-containing and butterfly-shaped crown compounds prepared at BYU. The butterfly-shaped crowns are two crown compounds connected together at two nitrogen atoms.



# A New Building Block Method To Synthesize Symmetrical and Asymmetrical Per-*N*-alkyl-Substituted Polyaza-Crown Compounds

Krzysztof E. Krakowiak,[†] Jerald S. Bradshaw,* Reed M. Izatt, and Daria J. Zamecka-Krakowiak

*Department of Chemistry, Brigham Young University, Provo, Utah 84602*

*Received February 7, 1989*

A new approach for the synthesis of a variety of per-N-alkylated polyaza-crown compounds is described. *N*-[2-(2-Chloroethoxy)ethyl]acetamide (**25**) and its benzamide analogue **26** are the key building blocks for the synthesis of the new polyaza-crowns. These chloroamides were reacted with primary amines or secondary diamines, followed by reduction of the resulting diamides, to produce polyamine intermediates containing two terminal *N*-ethyl or *N*-benzyl secondary amine functional groups. These secondary diamines were further reacted with dihalides in the presence of metal carbonates to form the polyaza-crowns. The overall yields for crown formation were generally very good. All of the new polyaza-crowns were prepared without the need for special nitrogen protecting reagents. Thus, the crowns were formed in a minimum number of steps. Twenty-three new polyaza-crowns containing from three to six nitrogen atoms in the macroring and from 16 to 36 ring members are reported.

**Figure 10.** First page of a paper describing a new synthesis of nitrogen-containing crown compounds. See Krzysztof E. Krakowiak and others, *Journal of Organic Chemistry* 54 (August 1989): 4061–67.

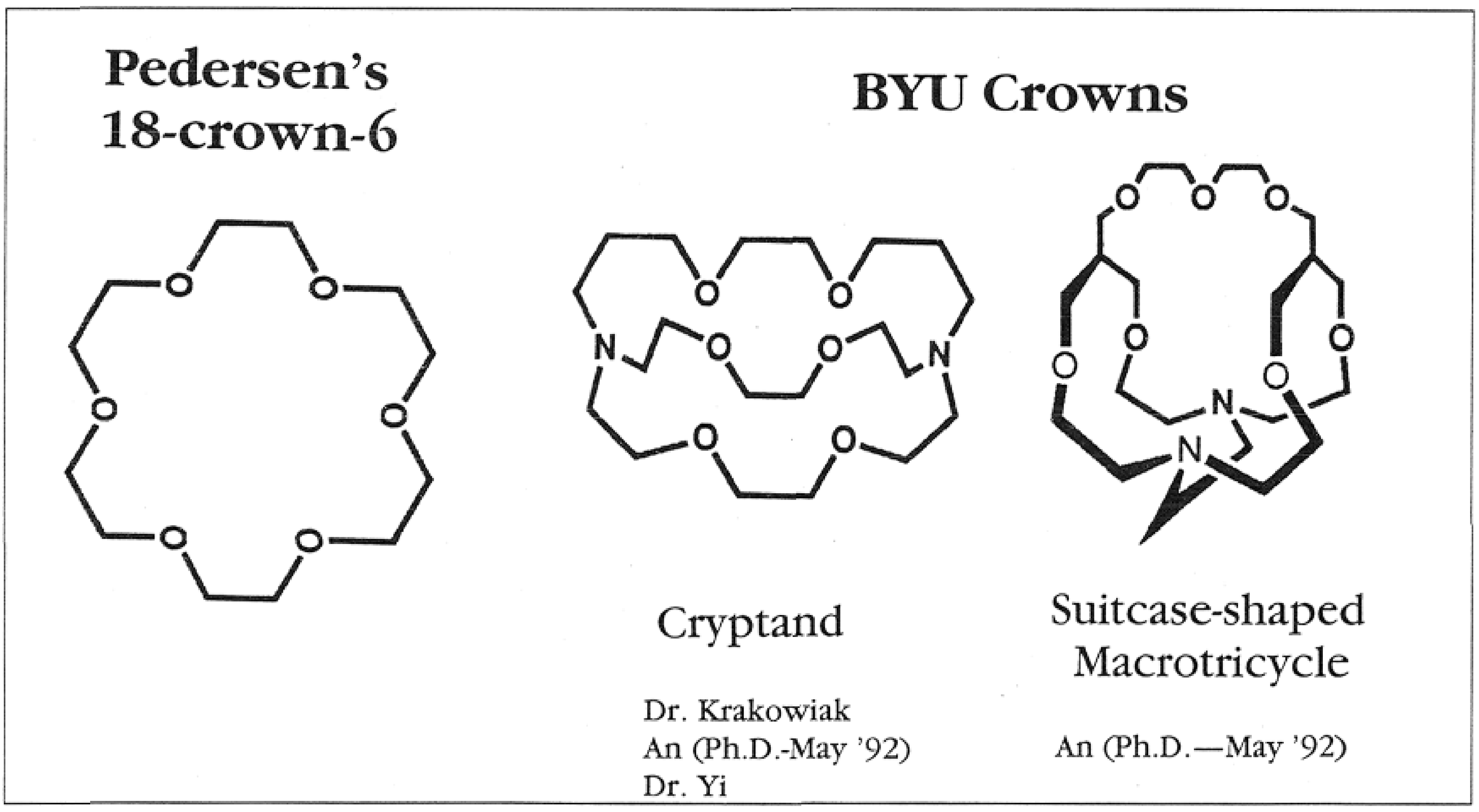


**Figure 11.** Structures representing the more complicated macrocycles prepared at BYU. The cryptand is shaped like an American football, while the macrotricycle is like a small overnight case.

What has been written so far is background for a most important new application of the crown compounds. The future of the crown-6 molecules is shown in figure 12. We have covalently attached a dinitrogen-containing 18-crown-6 compound to silica gel. Silica gel is similar to very fine sand. The crown compound is attached by very stable bonds between carbon, oxygen, and silicone (Si) atoms. Dr. Bryon Tarbot has attached many of these crown compounds to silica

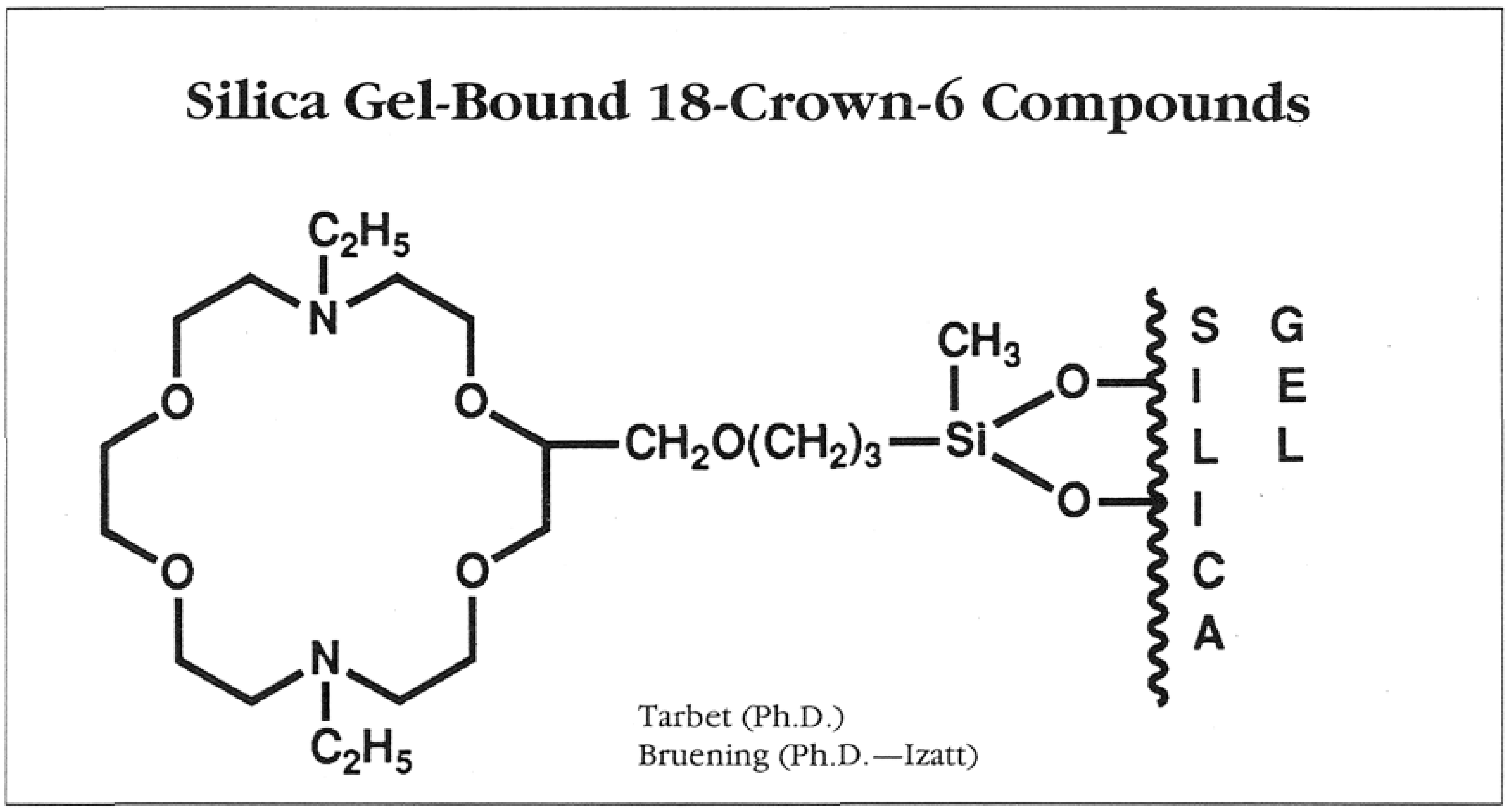


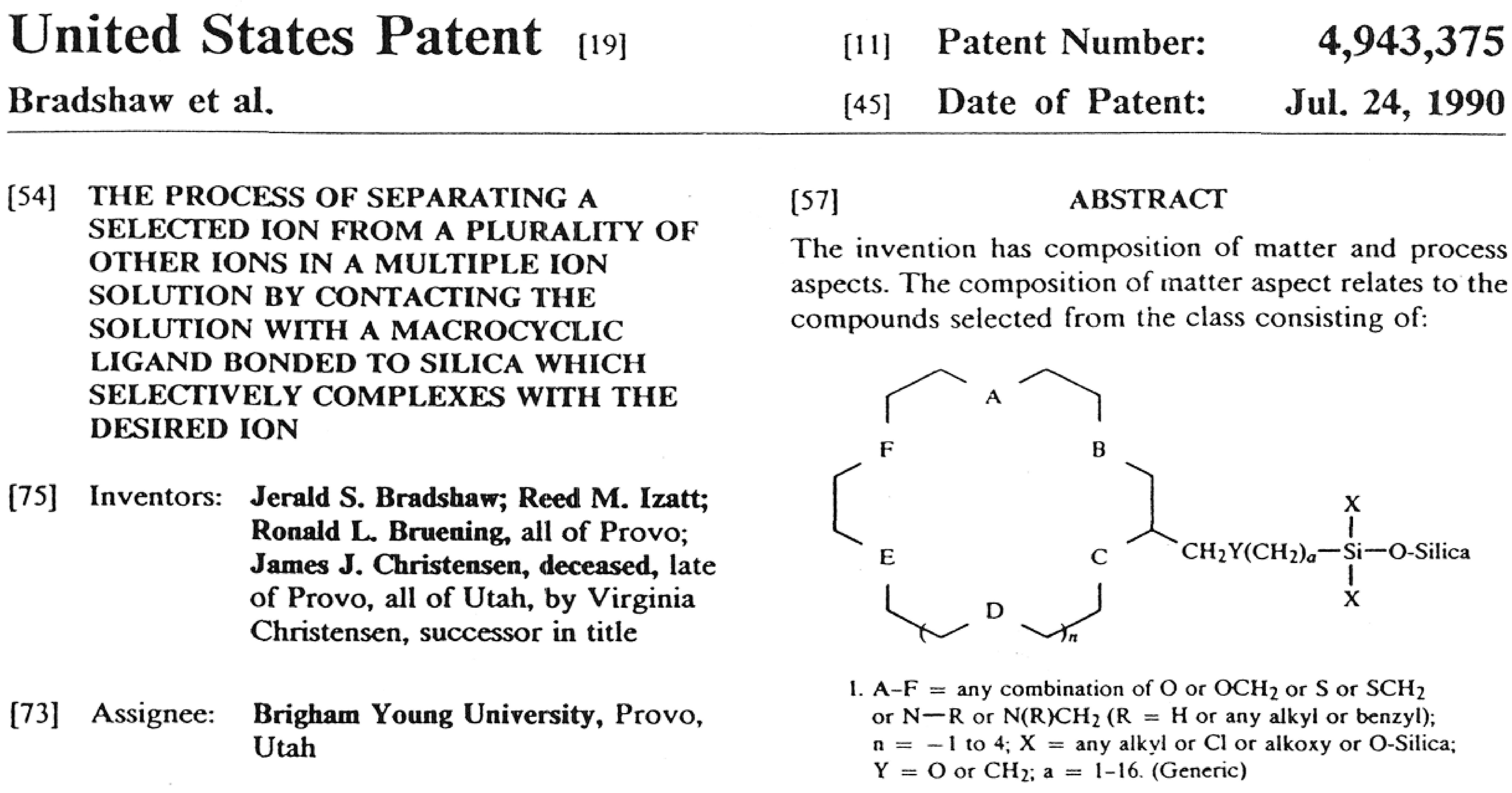
**Figure 12.** The structure of a dinitrogen-containing 18-crown-6 attached to the surface of silica gel. This material is very stable and can be used many times to remove metal salts from water.

gel. Dr. Ron Bruening, who works with Dr. Izatt, and his associates have studied the interactions of the silica gel-bound crown compounds with a variety of inorganic salts. They have found that the silica gel material shown in figure 12 interacts with lead, mercury, silver, and copper salts. The interaction is so strong that these salts can be removed from water. Thus, toxic lead can now easily be removed from drinking water. This process of removing metal salts from water is so important that we have received many patents.

Figure 13 shows the front page of a patent for "The Process of Separating a Selected Ion from a Plurality of Other Ions." This patent belongs to BYU, which has licensed this technology to IBC Advanced Technologies, Inc., where these processes are being developed for commercial use.

Figure 14 shows the separation of a copper salt from water. Dinitrogen-containing 18-crown-6 attached to silica gel, shown in figure 12, is in the column in A. Also shown in A is a liter of solution that contains a small amount of copper nitrate in water. Picture B in figure 14 shows the copper solution starting through the column. Notice the silica gel turns blue as the copper salt is absorbed. When copper interacts with a nitrogen-containing material, it forms a blue color. No copper is coming through the bottom of the column because all of the copper interacts with the dinitrogen-containing crown. Picture C in figure 14 was taken after all of the copper solution had passed through the column. The copper salts were completely retained on the dinitrogen-containing crown material. There has been much said about the problem of lead in drinking water. This silica gel material would completely remove lead or mercury salts from water. This could be an important future use of silica gel-bound crown chemistry. Sodium chloride, on the other hand, would not be removed by the column because this salt does not interact with the nitrogen-containing crown.

Removing the copper salts from solution is only part of the process. We may want to recover the copper, or at least we want to get it off the column so that we can use the expensive silica gel-bound crown material again. To remove the copper salt, we pass acid through the column. Acid interacts more strongly with the dinitrogen-containing 18-crown-6 than does copper. Picture D in figure 14 shows the acid solution going through the column. You can see how far the acid solution has passed because the gel is again white where the copper has been removed. Picture E shows the recovered solution which is a much darker color than at the beginning because



**United States Patent** [19]

**Bradshaw et al.**

[11] **Patent Number: 4,943,375**

[45] **Date of Patent: Jul. 24, 1990**

[54] **THE PROCESS OF SEPARATING A SELECTED ION FROM A PLURALITY OF OTHER IONS IN A MULTIPLE ION SOLUTION BY CONTACTING THE SOLUTION WITH A MACROCYCLIC LIGAND BONDED TO SILICA WHICH SELECTIVELY COMPLEXES WITH THE DESIRED ION**

[75] Inventors: **Jerald S. Bradshaw; Reed M. Izatt; Ronald L. Bruening,** all of Provo; **James J. Christensen, deceased,** late of Provo, all of Utah, by Virginia Christensen, successor in title

[73] Assignee: **Brigham Young University,** Provo, Utah

[57] ABSTRACT

The invention has composition of matter and process aspects. The composition of matter aspect relates to the compounds selected from the class consisting of:

1. A–F = any combination of O or $OCH_2$ or S or $SCH_2$ or N—R or $N(R)CH_2$ (R = H or any alkyl or benzyl); n = −1 to 4; X = any alkyl or Cl or alkoxy or O-Silica; Y = O or $CH_2$; a = 1–16. (Generic)

**Figure 13.** First page of U.S. Patent #4,943,375 describing the process of removing ions from water through the use of our crown macrocycles attached to silica gel. This patent belongs to BYU.

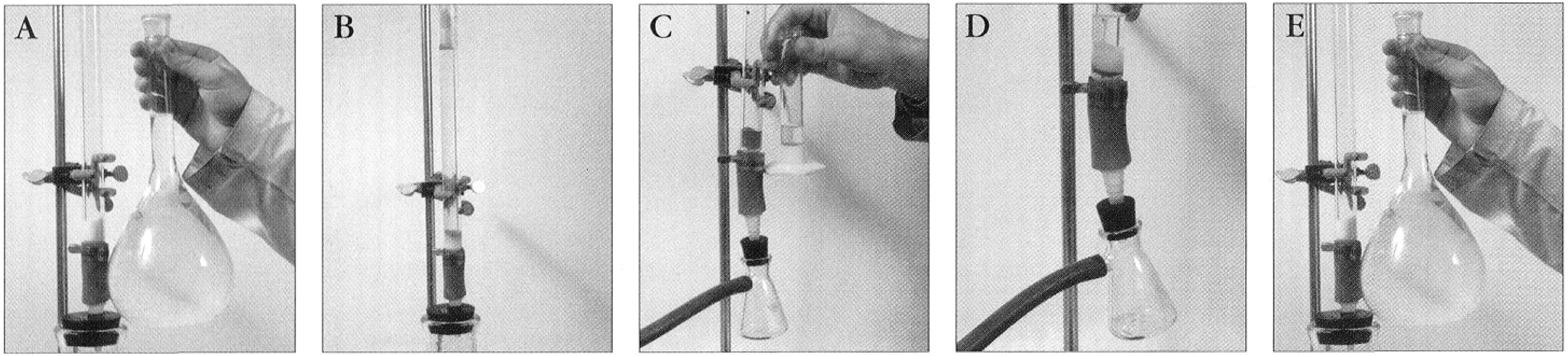


**Figure 14.** The separation of copper (Cu) from water and its recovery. (A) Copper-nitrate solution about to be poured through a silica-gel column of dinitrogen-containing crown. (B) Partially blue column showing the progress of the copper solution. (C) Blue column and clear solution indicating the copper salts were completely absorbed by the column. (D) Partially white column showing where acid has removed the copper. (E) The recovered solution, darker because the copper is more concentrated than it was in A.

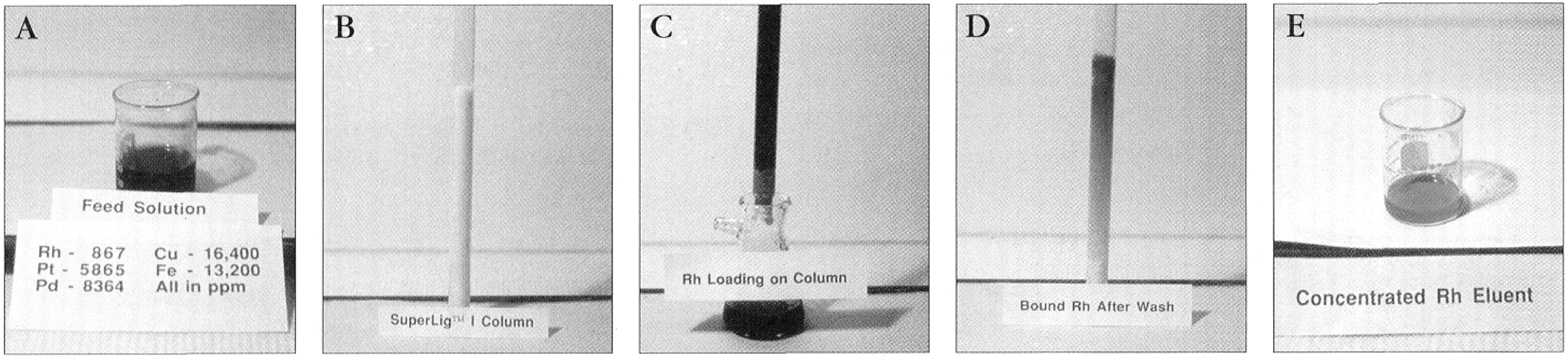


**Figure 16.** The removal and recovery of rhodium (Rh) from a mixture of 857 parts per million (ppm) of Rh, 5865 ppm platinum (Pt), 8364 ppm palladium (Pd), 16,400 ppm copper (Cu), and 13,200 ppm iron (Fe) in water.

it is more concentrated. Lastly in the total process, distilled water and a buffer solution are passed through the column to remove the acid. The column is then ready to be used again. This process is very expensive, but if one can use a column three or four hundred times, the cost is greatly reduced. The process can be used to remove the toxic and dangerous heavy metals such as mercury and lead from water in the same manner as shown in figure 14. We also believe this process could be used to remove radioactive plutonium and uranium from radioactive waste. Those materials would be concentrated and could be used again without the need for storage. This application has not been done in the laboratory, but it should be possible.

Figure 15 (next page) is an artist's concept of this process. The large irregular circles at the edges are silica gel particles with the dinitrogen-containing 18-crown-6 (small circles) sticking out. Remember the crown interacts strongly with mercury (Hg) salts. Sodium (Na) and mercury nitrates in water are passed through the column. The 18-crown-6 reaches out and grabs the mercury (second diagram in figure 15). The dinitrogen-containing crown does not interact with the sodium, so the sodium salt comes through. One can see the mercury going into the cavity, where it stays. Thus, mercury and sodium have been separated. To remove the mercury, acid is passed through the column. In the last diagram of figure 15, we see the acid reacting with the crown and thereby pushing the mercury out.

Figure 16 (facing page) shows another colorful separation that is important to each of us. Rhodium is an important (and expensive) metal that is used in the catalytic converter in our automobile exhaust systems. The rhodium helps to convert any unburned gasoline in the exhaust into carbon dioxide. It is important to recover these expensive metals. The black mess in picture A of figure 16 is an acid solution of rhodium (Rh), platinum (Pt), palladium (Pd), copper (Cu), lead (Pb), and iron (Fe) salts. This is a typical solution prepared from spent catalyst. These materials are present in parts per million (ppm) amounts. If there were 867 people at my lecture, they would constitute 867 parts of the million people that live in Salt Lake County—a very small number. Picture B shows a column with a special material attached to silica gel that interacts only with the rhodium. All other metal salts pass through this column. This is called a SuperLig®. Picture C shows the column after all the black mess has passed through it. It is still black because of the small amount of solution still on the column. In Picture D we see the column after the excess metal ions were removed by passing some acid through the column. Notice

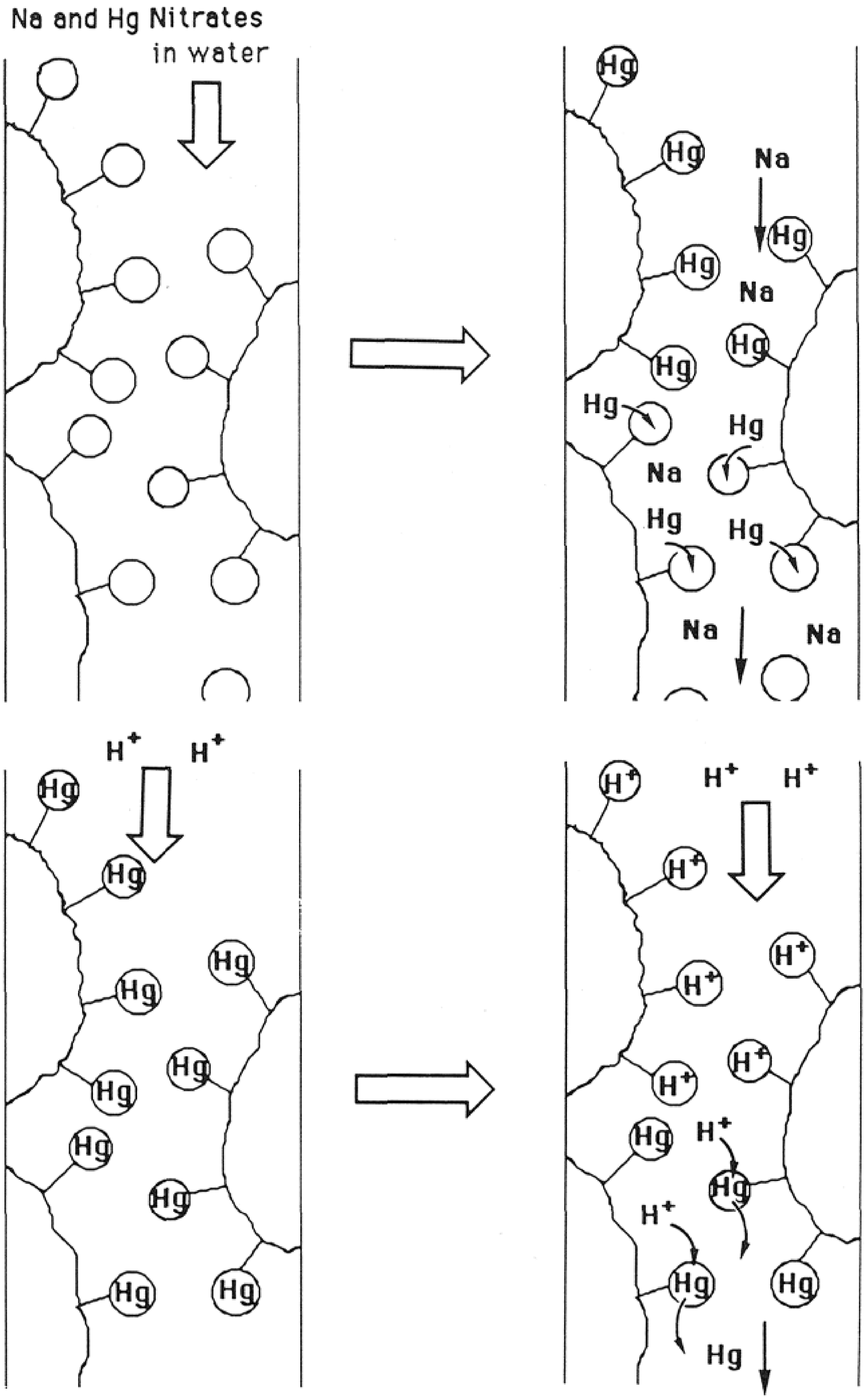


**Figure 15.** An artist's concept of the separation and removal of mercury ions (Hg) from sodium (Na). The large irregular shapes at the edges represent silica gel containing the dinitrogen-crown (small circles). A mixture of Hg and Na nitrates in water is added, and the Hg is trapped by the crown (upper two figures). Then acid ($H^+$), which interacts more strongly with the crown than does Hg, pushes the Hg out of the column (lower two figures). The silica gel can then be neutralized ($H^+$ removed) and used again.

the beautiful red color of Rh on the column. The rhodium is 99.9% pure; all the Rh in the original sample is on the column. All of the platinum, palladium, copper, lead, and iron salts passed through this column. Rh is removed from the column with a solution that interacts more strongly with it than does the material attached to the silica gel. We see the pure Rh solution in picture E. This process works. The rhodium recovery procedure is in the pilot plant stage in precious metal refineries all over the world.

The 18-crown-6 compounds are interesting new chemicals. Their ability to interact with inorganic salts make them important new materials to inexpensively remove toxic heavy metals from water. Radioactive elements could also be removed from radioactive waste, an application which would help solve that world-wide problem. Valuable precious metals that are important in our society can be recovered and purified. We have a great knowledge in our laboratory of the interactions of various materials with the crown compounds. All we need to do is couple this knowledge with good research to make materials that will further help mankind.

## NOTES

In addition to those acknowledged on p. 37, Dr. Bradshaw thanks the following people who have helped make research at BYU enjoyable: a great group of undergraduate, graduate, and postdoctoral research associates whose names are given in the relevant figures; outside funding agencies including N.S.F., D.O.E., Naval Research, and the Utah Centers of Excellence Program; the chemistry department chairmen over twenty-five years, most recently J. B. Ott and E. M. Woolley; great support people in the Chemistry Department including Martin Ethington, Gary Reynolds, Kelly Jensen and his staff, Ivan Cook and his staff, Richard Meibos and Guy Curtis and their staff, all department secretaries (past and present), Jerry Mason, Janet Curtis, Bruno Szalkowski, and Que Adams and his staff.

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