Second Progress Report for AEC Contract AT(04-3)34, P. A. 218

MULTIHETEROMACROCYCLES THAT COMPLEX METAL IONS

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MASTER

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The 1974-1975 Research Accomplishments

Supported by ERDA Contract AT(04-3)34, P. A. 218

Abstract

The overall objective of this research is to design, synthesize and evaluate cyclic and polycyclic host organic compounds for their abilities to complex and lipophilize guest metal ions, their complexes and clusters. Host organic compounds consist of strategically placed solvating, coordinating and ion-pairing sites tied together by covalent bonds through hydrocarbon units around cavities shaped to be occupied by guest metal ions, or metal ions plus their ligands. Specificity in complexation is sought by matching the following properties of host and guest: cavity and metal ion sizes; geometric arrangements of binding sites; numbers of binding sites; characters of binding sites; valences. In the 20.5 months since the inception of this contract (1 May 1974) and in the remaining 3.5 months of this project year, the specific goals and accomplishments are as follows. (1) We have synthesized in small quantities and have characterized macrorings $(OCH_2CH_2OCH_2COCH_2COCH_2)_2$ and $(OCH_2CH_2OCH_2COCH_2COCH_2)_3$. Molecular models of the former compound indicate six oxygen coordinating sites (and two negative charges) are available, and of the latter compound nine oxygen coordinating sites (and three negative charges) are available to metal ion guests. The smaller cycle possesses stability constants in dioxane-water at 25° that indicate it complexes divalent metals at least 1.9 powers of ten better than the open-chain model, $CH_3OCH_2COCH_2COCH_2OCH_3$. The order in which the metal ions are better complexed by the cycle are $Cu^{2+} \sim UO_2^{2+} > Ni^{2+} \stackrel{\sim}{>} Fe^{2+} \sim Co^{2+} \sim Zn^{2+} \sim Cd^{2+} > Mn^{2+}$. The complexes of UO_2^{2+} and Cu^{2+} (chloroform soluble) have been isolated and characterized. The larger cycle complexes trivalent metals 0.9 to 1.7 powers of ten better than the open-chain model compound. The order is $La^{3+} \sim Ce^{3+} > Cr^{3+}$.

Complexation was very fast except with UO_2^{2+}. (2) Attempts to synthesize a macrocycle composed of six 1,3-linked aryl groups (each containing a methoxyl or hydroxyl group in the 2-position to compose a six-oxygen cage of zero to 6 valence potential) have not yet been successful. (3) We have synthesized five macrocycles of the structures indicated in which R = CH_3.
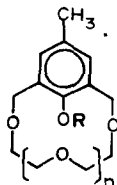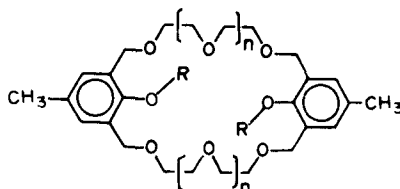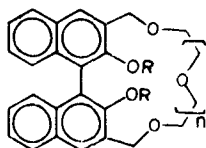

n = 2; n = 3; n = 4   n = 0; n = 1

Their binding constants in chloroform with sodium, potassium, ammonium and cesium picrates have been measured. The higher binding constants are found when the diameter of the ions best fit the diameters of the holes. (4) Six compounds containing one macroring and two inward-pointing ArOH or $ArOCH_3$ groups have also been

n = 2, R = H or CH_3;
n = 3, R = H or CH_3;
n = 4, R = H or CH_3

prepared, characterized and tested for their binding ability toward lithium, sodium, potassium, rubidium and ammonium picrates. (5) Racemic compounds containing two binaphthyls and four inward-turning methoxyls have been prepared and characterized, as has its sulfur analog containing four inward-turning hydroxyl
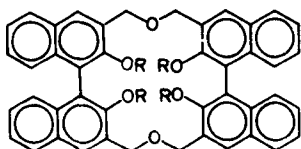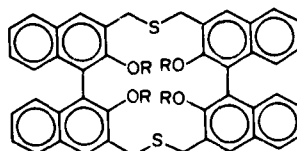

R = CH_3 R = H

groups. These compounds have not yet been tested in their metal ion binding abilities. (6) Cage-shaped multiheteromacrocycles have been prepared that possess the meso, racemic and (RR) structures of the compound containing ten oxygen ligand sites and the (RR)-isomer of the compound containing four sulfur and six oxygen ligand sites. The racemic isomer of the fully oxygen compound binds potassium picrate over a power of ten better in chloroform than sodium
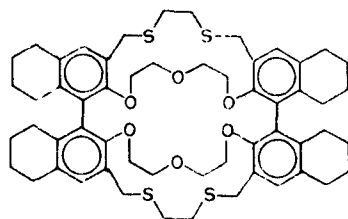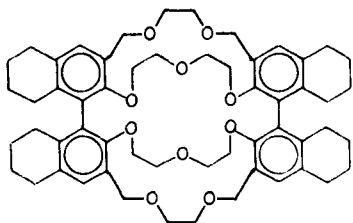
and two powers of ten better than cesium or lithium picrates. The interesting question of whether the potassium ion is inside the almost fully surrounded egg-shaped hole has not yet been answered. (7) Two ring systems with the polarized oxygens of two phosphonate ester groups located above and below their holes have been prepared, but not tested for their metal binding abilities. Their corresponding acids have not yet been prepared.
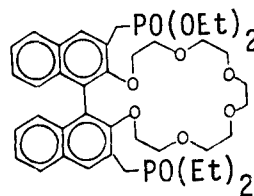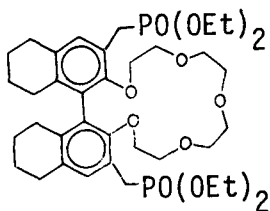
The synthetic part of the project has prospered more than the testing part for two reasons. (1) The synthetic part had to precede the testing part. (2) The syntheses were exploratory and involved many steps, and only amounts required for characterization were obtained in many cases.

Personnel

1. The principal investigator (Donald J. Cram) devoted one full-time summer month and 20% of each of the nine academic months to the project.

2. Dr. Roger C. Helgeson, Assistant Research Chemist I, was employed 87% of full time on this project. He has had seven postdoctoral years' previous experience in the synthesis of macroring compounds, three of which were with multiheteromacrocycles.

3. Dr. Karl Koenig, Postgraduate Research Chemist I, was employed formally 86% of full time on this project. He obtained his Ph.D. degree in 1974 at the University of Southern California.

4. Dr. Albert Alberts, Postgraduate Research Chemist I, was employed formally 86% of full time on this project. He obtained his Ph.D. degree in 1974 at the University of Groningen.

Drs. Koenig and Alberts actually devoted full time to this project, but there were insufficient funds to pay them full time. Dr. Helgeson worked part time on other projects (for lack of funds on this one). Research costs have increased drastically and out of proportion to the general inflation.

Research Results

A. Syntheses and Complexation of Multiheteromacrocycles Containing
β-Diketonide Units (with Dr. Albert Alberts)

Since β-diketonides are excellent ligands for a variety of metals, we have incorporated these units into cycles to provide both binding site and valence control. The synthetic sequences used are formulated. The cyclization yields were good, but the unmasking reactions in which the thioketals were converted to the diketones went only moderately well, owing to the instability of the cycles to the conditions of the unmasking reaction.

$$TsO(CH_2CH_2O)_2Ts \xrightarrow{} NaH$$
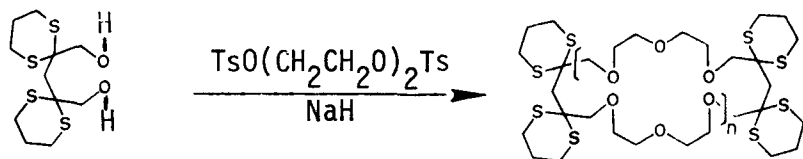
1

2, n = 1 (64% yield);

3, n = 2 (29% yield)

1) HgCl$_2$, CdCO$_3$
CH$_3$OH

2) H$_3$O$^+$
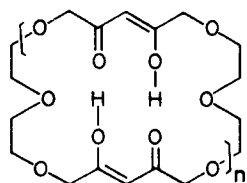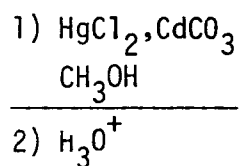
4, n = 1 (24% yield);

5, n = 2 (16% yield)
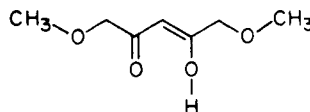
6

A convenient method was adopted for determining stability constants of these macrocycles at 25° in dioxane-water (one-to-one by volume) compared to the open-chain reference compound 6. The procedure was taken from M. Calvin and R. Wilson, <u>J. Amer. Chem. Soc</u>., 67, 2003 (1945). Table 1 lists the results with the cycle containing two acetylacetone units, 4, and with the open-chain model compound, 6.

Table 1. Relative Stability Constants at 25°

in Dioxane Water (One-to-One by Volume)

Ion	Cycle with two acetylacetone units (4)			Open-chain model compound, 6			pH	$\log(K_c/K_0)^a$ $-\Delta pK_{av}$
	pK_1	pK_2	pK_{av}	pK_1	pK_2	pK_{av}		
Cu^{2+}	8.2	7.8	8.0	8.2	7.7	8.0	1.0 - 2.5	---
UO_2^{2+}	8.2	7.8	7.9	8.2	7.7	8.0	1.0 - 2.5	---
Fe^{2+}	8.1	7.1	7.7	6.2	4.8	5.4	2.5 - 5.5	2.3
Ni^{2+}	8.0	6.7	7.5	5.8	4.4	5.1	2.5 - 6.0	2.4
Co^{2+}	7.8	6.3	7.1	5.4	4.2	4.8	3.0 - 6.5	2.3
Zn^{2+}	7.0	5.5	6.3	4.6	3.4	4.0	3.5 - 7.5	2.3
Cd^{2+}	6.2	5.0	5.8	4.1	2.9	3.4	4.0 - 8	2.3
Mn^{2+}	5.1	3.8	4.4	3.6	1.9	2.5	4.5 - 9	1.9

[a] Ratio of stability constant of cycle (K_c) to that of open-chain model (K_0).

With this technique, the $\log(K_c/K_0)$ values for Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Mn^{2+} were measurable and ranged from 2.4 to 1.5. Those for Cu^{2+} and UO_2^{2+} were not measurable since these ions have such a high affinity for both the cycle and the open-chain model. Clearly the cycle is a much better binder than the model for all of the ions measured. The same is probably even more true for Cu^{2+} and UO_2^{2+}. Equilibration was instantaneous in all cases except UO_2^{2+}, which took three hours to equilibrate. Solvent extraction experiments were carried out with two-unit cycle 4 dissolved in chloroform, and Co^{2+}, Cu^{2+} and UO_2^{2+} in water. The ions were readily extracted (UO_2^{2+} slowly over a five-hour period), and the complexes formed were isolated and characterized. Elemental analysis indicated that no additional ligands were present, and that the complexes were one-to-one. Table 2 indicates their physical properties. These facts suggest they possess structure 7. The complexes of Cu^{2+} and UO_2^{2+} appeared to be more stable than the others.
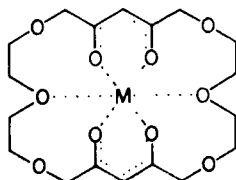
$\underset{\sim}{7}$

Table 2. Physical Properties of Complexes of Metal Ions

M^{2+}	Color	M.p.(dec.)^{o}C	IR(C=O)cm^{-1}
Cu^{2+}	green	196	1580
Co^{2+}	violet	132	1585
UO_2^{2+}	orange	153	1583

Table 3 lists the results of comparisons of binding abilities of the cycle containing three acetylacetone units (5) with those of the open-chain model (6) toward Cr^{3+}, Ce^{3+} and La^{3+}. The enhancement in stabilities of the complexes of the cycle with three units is smaller than that with two, but is still substantial.

Table 3. Estimated Relative Stability Constants at 25°

in Dioxane-Water (One-to-One by Volume)

Ion	Cycle with three acetylacetone units (5)			Open-chain model compound, (6)			pH	$\log(K_c/K_o)^a$ $\sim \Delta pK_2$
	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3		
Cr^{3+}	7.8	6.8	5.9	7.2	5.9	4.8	1.5 - 6	0.9
Ce^{3+}	6.6	4.9	2.0	4.6	3.2	1.8	3.5 - 9	1.7
La^{3+}	6.9	5.1	2.7	4.7	3.4	2.1	3.0 - 8	1.7

^{a}Estimated ratio of stability constant of cycle (K_c) to that of open-chain model (K_o).

In a preliminary transport experiment, it was found that Fe^{3+} could be transported through a chloroform bulk liquid membrane containing the three-unit cycle 5 from one aqueous solution to another (a $\bigcup$-tube experiment).

B. Progress Toward the Synthesis of Metahexaphenyl Compounds (with
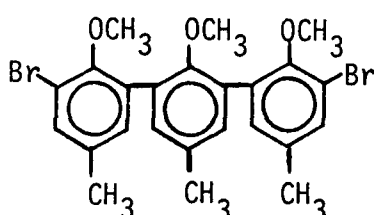
Dr. Karl Koenig)

Attempts to synthesize the cyclic metahexaphenyl compounds 11 have so far failed. Compound 8 failed to give cyclic products in attempted coupling reactions. Compound 9 was synthesized in only 1% overall yield after many attempts. A good synthesis (60% overall from p-cresol) of 10 has been developed, but thus far the compound has resisted coupling leading to cycle, although only three attempts have been made to date. Better cyclization methods are needed.
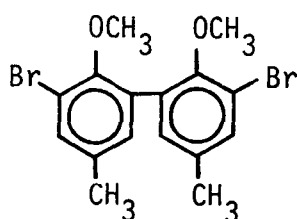
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9
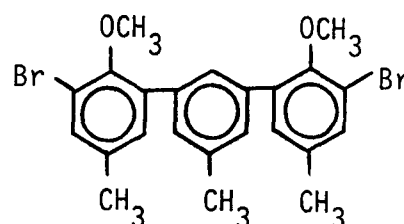
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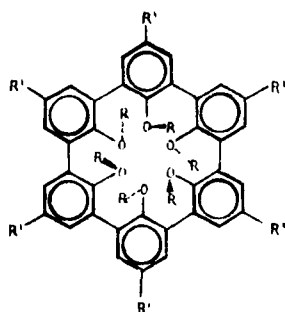
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C. Synthesis and Complexation of Multiheteromacrocycles Containing

Inward-Turning Methoxyphenyl Units (with Dr. Karl Koenig)

Methods were developed for making starting materials 12 and 13 in good

yields, which in turn were converted to cycles 14-18 by treatment at 25° with the

appropriate diols and sodium hydride in dry tetrahydrofuran (THF). In each case,

a solution of diol and dihalide in dry THF was added to a stirred mixture of sodium

hydride and dry THF. Yields of 14-16 varied from 20 to 80% and those of 17 and 18

from 14-26%. Dihalide 13 was the better starting material.

12

13
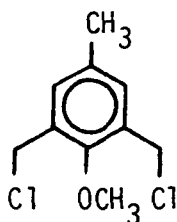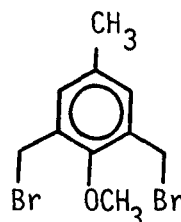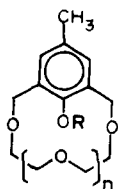
14, n = 2, R = CH_3 17, n = 0, R = CH_3
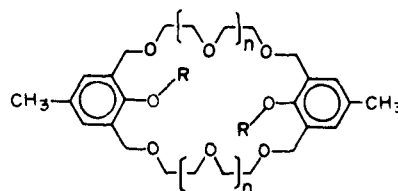
15, n = 3, R = CH_3 18, n = 1, R = CH_3

16, n = 4, R = CH_3

Semiquantitative binding constants for compounds 14-18 and metal picrates in chloroform were obtained by shaking 0.10 ml of chloroform, 0.075 M in cycle, with 0.50 ml of water, 0.015 M in lithium, sodium, potassium or ammonium picrate, or with 0.75 ml of water 0.010 M in rubidium or cesium picrate. The amounts of picrate ion drawn into the chloroform layer by the cycle and the amounts of picrate left in the water were measured spectrophotometrically (uv). Control experiments demonstrated that no cycle was drawn into water and that in the absence of cycle no picrate salt was drawn into chloroform. The binding constants were calculated assuming that complexation was one-to-one. Table 4 reports the results (compounds 19 and 20 prepared and studied by others for other purposes are included for comparison).
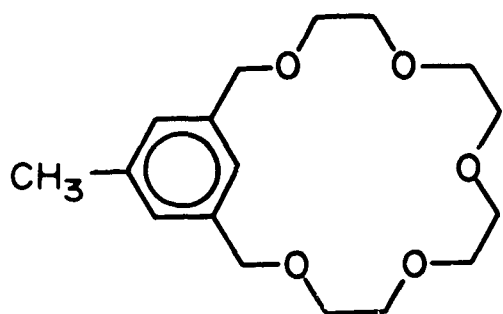
Table 4. Estimated Association Constants
of Picrate Salts with Cycles in Chloroform at 25°

Cycle no.	Number groups in cycles		Total	K_a values x 10^{-3}					
	OCH_3	CH_2OCH_2	O ligands	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
14	1	4	5	3.8	14.0	20.7	---	4.9	4.6
15	1	5	6	9.9	47.4	1,750	---	115	280
16	1	6	7	2.8	46.7	181	---	655	100
17	2	4	6	0.83	1.9	3.7	1.7	1.9	1.4
18	2	6	8	0.49	5.0	8.6	4.2	6.0	6.3
19	0	5	5	1.2	2.4	78.9	---	37.9	54.2
20	"1"	5	"6"	20.0	914	1,180	---	480	380
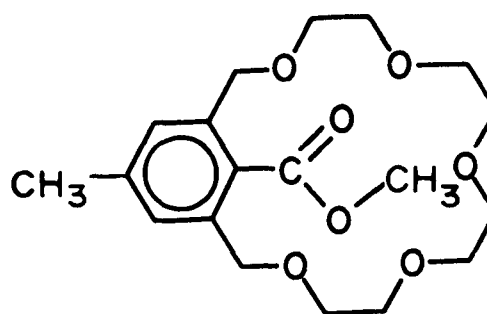
19   20

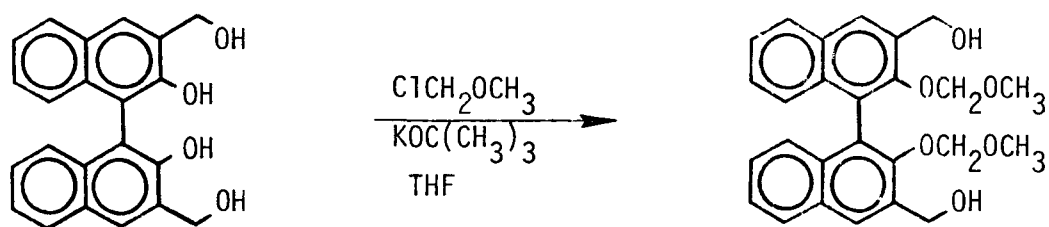Conclusions drawn from the data are as follows. (1) For the cycles containing one aryl there is a rough correlation between the ion diameter and the hole size (Corey-Pauling-Koltun molecular models) in that conformation in which the aryl plane and that of the ring oxygens is $> 30°$. This conformation allows the O of OCH_3 groups and that of $C = O$ (in 20 only) to act as an additional non-coplanar ligand for a metal ion. (2) The cycles containing two aryls (17 and 18) are almost always the poorest ligands for all ions. The aliphatic ether ligand is superior to the alkoxyaryl ligand toward these hard cations. (3) In comparably sized cycles 15, 19 and 20 (18-ring membered), 2-aryl substituents fall in the order $CO_2CH_3 > OCH_3 > H$ in enhancing binding toward all ions except K^+, for which the order is $OCH_3 > CO_2CH_3 > H$. (4) Of the ions, lithium shows the least sensitivity to the ligand character (varied only by a factor of 40), and the other ions show about the same spread of factors of about 250 to 500.
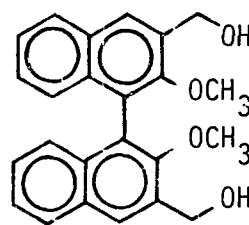
   D. Synthesis and Complexation of Multiheteromacrocycles Containing One
      Inward-Turning 2,2'-Dimethoxy- or 2,2'-Dihydroxy-1,1'-binaphthyl
      Units (with Drs. Roger Helgeson and Karl Koenig)

      Compounds 24-29 were prepared in 15-40% yields from key starting
materials 21-23 by treatment with the appropriate polyether ditosylates and
sodium hydride in dry tetrahydrofuran.

21

$\xrightarrow[\text{THF}]{\overset{\text{ClCH}_2\text{OCH}_3}{\text{KOC(CH}_3)_3}}$

22 (55% yield)

$\xrightarrow{\text{CH}_3\text{I, K}_2\text{CO}_3, \text{(CH}_3)_2\text{CO}}$

23 (90% yield)

$23 + \text{TsO(CH}_2\text{CH}_2\text{O})_3\text{Ts} \xrightarrow{\text{NaH}} 24$, R = CH$_3$, n = 2 (40% yield)

$23 + \text{TsO(CH}_2\text{CH}_2\text{O})_4\text{Ts} \xrightarrow{\text{NaH}} 25$, R = CH$_3$, n = 3 (40% yield)

$23 + \text{TsO(CH}_2\text{CH}_2\text{O})_5\text{Ts} \xrightarrow{\text{NaH}} 26$, R = CH$_3$, n = 4 (20% yield)

$22 + \text{TsO(CH}_2\text{CH}_2\text{O})_3\text{Ts} \xrightarrow{\text{1) NaH 2) H}^+} 27$, R = H, n = 2 (40% yield)

$22 + \text{TsO(CH}_2\text{CH}_2\text{O})_4\text{Ts} \xrightarrow{\text{1) NaH 2) H}^+} 28$, R = H, n = 3 (30% yield)
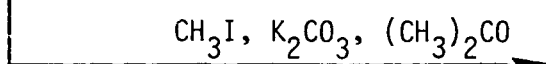
$22 + \text{TsO(CH}_2\text{CH}_2\text{O})_5\text{Ts} \xrightarrow{\text{1) NaH 2) H}^+} 29$, R = H, n = 4 (15% yield)

These six compounds were examined for their abilities to bind picrate salts by the same method described under Section C. Table 5 gives the approximate association constants.

Table 5. Estimated Association Constants

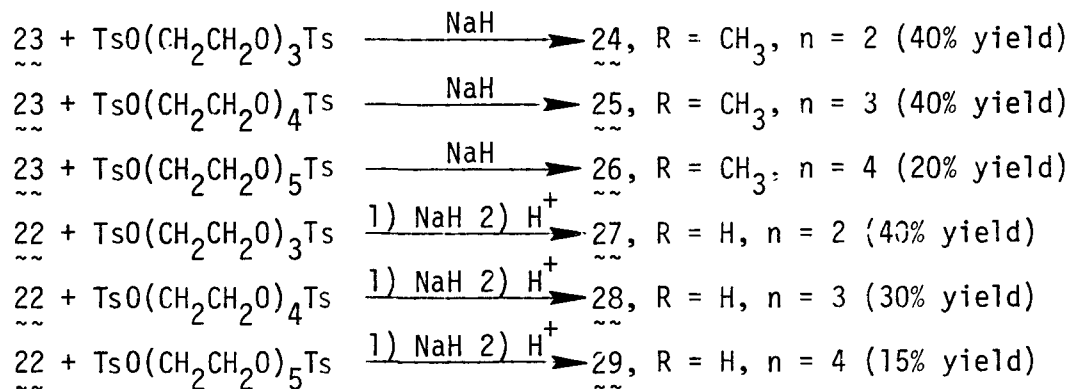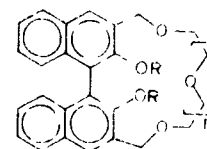of Picrate Salts with Cycles in Chloroform at 25°

Cycle no.	Number groups in cycles			Total O ligands	K_a values x 10^{-3}					
	OCH_3	OH	CH_2OCH_2		Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
24	2	0	4	6	16	1,270	3,600	---	561	624
25	2	0	5	7	19	43	927	976	955	368
26	2	0	6	8	13	33.5	223	194	362	86
27	0	2	4	6	2.2	8.0	18	---	11.0	4.3
28	0	2	5	7	7.1	15.5	232	222	197	53
29	0	2	6	8	4.8	31	104	87	224	38

The K_a values of the hydroxyl-containing cycles 27-29 did not change when the pH of the aqueous solution extracted was changed from the normal of about 7 to about 4 by addition of hydrochloric acid. Thus the extraction does not seem to involve aryloxide formation, and the cycles with their two hydroxyl groups intact are involved in complexation. We have not yet tested the complexing ability of 27, 28 and 29 toward divalent metals using the technique applied to the acetyl-acetone cyclic compounds of section A.

The conclusions drawn from the results of Table 5 are as follows. (1) The methoxyl-containing cycles are better than the hydroxyl-containing cycles as ligand assemblies. Intramolecular hydrogen bonds must be broken to complex the latter but not the former compounds. Furthermore, the electron-releasing character of methyl as compared to hydrogen should make the oxygens of the methoxyl group more basic than the oxygens of the hydroxyl groups. These effects appear more important than steric inhibition of complexation that might be associated with the methoxyl-containing compounds. (2) With almost every cyclic ligand,

the larger metal ions (K^+, Rb^+ and Cs^+) are better complexed than the smaller (Li^+ and Na^+). The bias of the systems for larger ions probably arises out of the enforced distance from each other of the two benzyl oxygens, a distance spannable only by the larger ions. The fits between Corey-Pauling-Koltun molecular models of 24, 25 and 26 and a series of graded ball bearings (models for metal ions) have been examined. The ionic diameters of the metal ions that are assumed are those of Pauling (Li^+, 1.20 Å; Na^+, 1.90 Å; K^+, 2.66 Å; Rb^+, 2.96 Å; Cs^+, 3.38 Å). The four bridging oxygens in the model of 24 are close to being coplanar, while one methoxyl oxygen is somewhat above, and the other somewhat below the plane. In molecular and ion models, the best fit for 24 is with K^+ (Rb^+ is good, Cs^+ is marginal, Na^+ can touch five of the six oxygens with ring folding, and Li^+ is poor); 25 best fits Cs^+ (with some folding, Rb^+ fits, but K^+ and Na^+ are successively worse, since the bridge is not long enough to fold much); 26 to gather the oxygens around its hole must fold, and seems to be able to fold equally well for Cs^+, Rb^+ and K^+, but cannot fold nearly enough for Na^+ or Li^+. The experimental results and the expectations based on model examination correspond reasonably well except for Na^+ complexation with 24. Molecular model examination suggests that the gathering of two cycles around one metal ion is sterically hindered by the methoxyl groups. (3) The additional structuring potential of 27-29 due to intramolecular hydrogen bonding makes the complexation results with these cycles interpretable. Molecular models of all three cycles indicate that each OH group is best located to hydrogen bond the second oxygen from the arylmethylene. Such a structure for 27 is rigid and prevents the oxygens from gathering around a metal without breaking the hydrogen bonds. As the chain gets longer, even the hydrogen bonded structures become more flexible,

and more oxygens can gather around ions. The data indicate that 27 is a very

poor ligand for any metal, but 28 and 29 become fairly good ligands for the

larger metal ions.

E.   Compounds that Include Two Binaphthyl Groups in Macrorings and Possess

Four Inward-Turning Hydroxyl or Methoxyl Groups (with Drs. Roger

Helgeson and Karl Koenig)

Molecular models of compounds such as 32 and 35 indicate the four

oxygens directly bonded to the naphthalene ring could become bound tetrahedrally

to ions such as U^{4+}. Compound 32 (as a mixture of racemic and meso isomers)

was prepared from 30 and 31 (available from other studies) in 60% yield.

30   31   32 (R = CH_3)
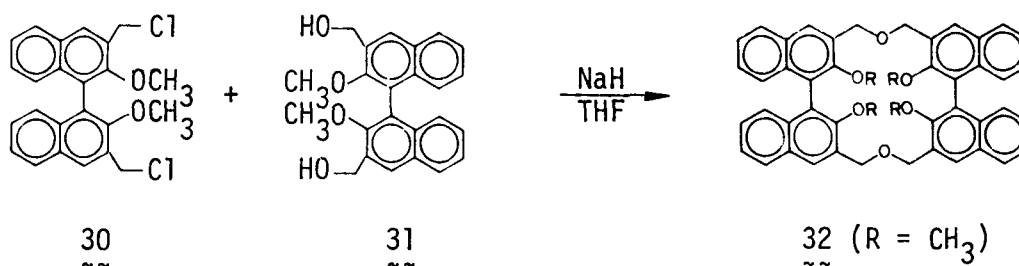
Thus far we have not been successful in preparing the more desired compound

with the structure of 32 with R = H. Compound 32 has not yet been tested in

any metal-binding experiments.

However, compound 35 has been prepared (as a mixture of racemic and

meso isomers) and does have the four hydroxyl groups turned toward one another

to provide (when ionized) counterions for metal ions. The ring-closing reac-

tion to give the ring system involved 33 and 34 (available from other studies)

as starting materials, and it went in 30% yield. Hydrolysis of the diacetate

produced initially went in 70% yield to give 35. Compound 35 has not yet

been tested in any metal-binding experiments.

33 + **34** → **35** (R = H)
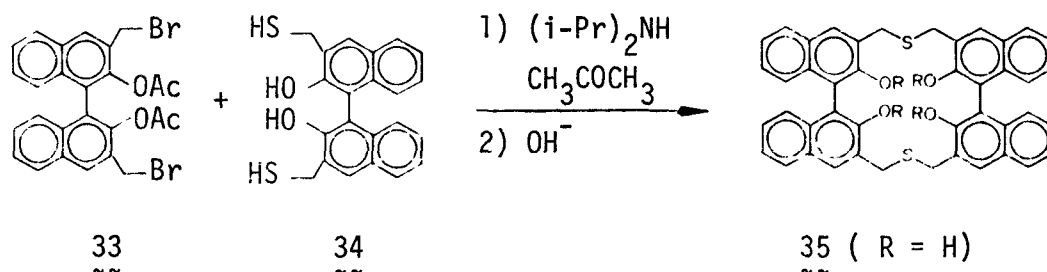
F. Preparation and Preliminary Testing of Two Cage Compounds in which

 Two Binaphthyl Units are Bound Together by Four Strands (with

 Dr. Roger Helgeson)

Lehn's cryptates [J. M. Lehn, Structure and Bonding, 16, 1 (1973)] are three-stranded bicycles of ethyleneoxy units tied together by binding to two nitrogen atoms. The cryptates have shown the greatest selectivity toward metal ions of any ligand assemblies yet prepared. The length of the three strands controls the hole size, and the metal ions once inside are surrounded on all sides by electron pairs. We have prepared two kinds of four-stranded cage compounds, 38 and 39.

Compound 36 (available from other studies) was chloromethylated to give 37 in 70% yield. Treatment of 37 with ethyleneglycol gave 38 in 40% yield.

36 → **37**
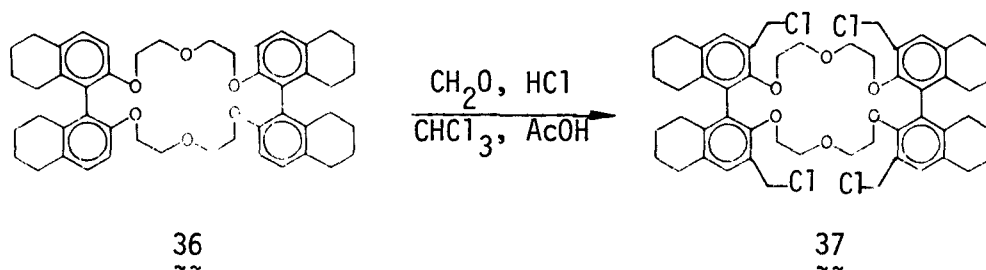
When treated with 1,2-ethanedithiol, 37 gave 39 in 25% yield. The meso, racemic and (RR)-isomeric forms of 38 have all been made and characterized, as has the (RR)-isomeric form of 39.

$$37 + HO\frown OH \xrightarrow[\text{THF}]{\text{NaH}}$$

38

$$37 + HS\frown SH \xrightarrow[\text{THF}]{\text{NaH}}$$

39
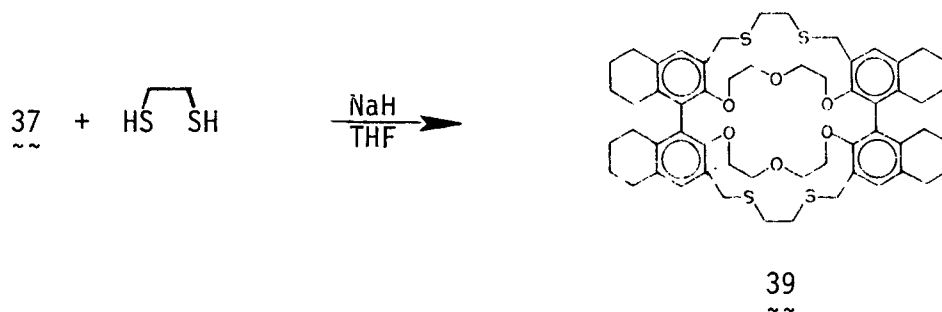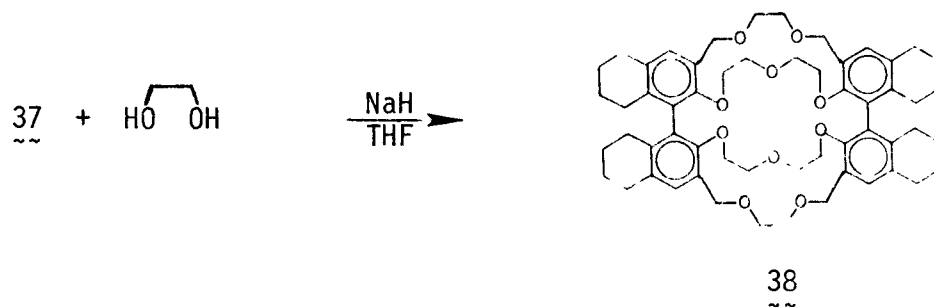
The cage shape of these compounds can be better appreciated by the three-dimensional representation of (SS)-38. The central egg-shaped cavity is surrounded by ten oxygen atoms with their electron pairs turned inward. The compound possesses D_2 symmetry (three mutually perpendicular C_2 axes).
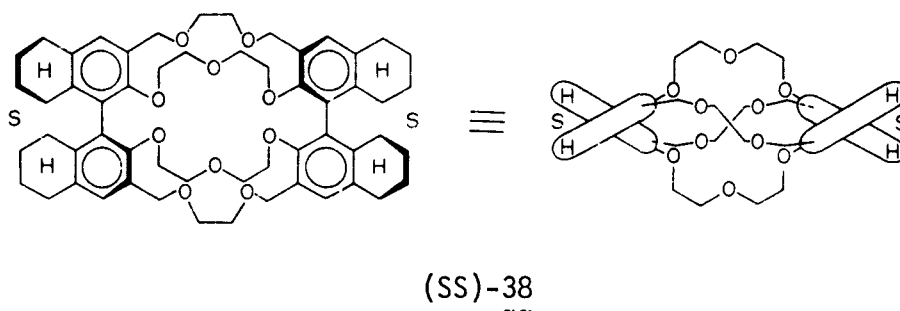

(SS)-38

The binding constants of racemic 38 (composed of the enantiomers (RR)-38 and (SS)-38) toward metal and ammonium ion picrates in chloroform (see Section C for method) are as follows: Li^+, 3.1×10^3; Na^+, 51.5×10^3; K^+, $4,000 \times 10^3$; Cs^+, 5.1×10^3; NH_4^+, 74×10^3. Examination of molecular models of (SS)-38 (or (RR)-38) and those for the metal ions and ammonium ion indicate

that all cations can enter and leave the cage but Cs^+, which only can coordinate on one of the four outside faces of the cage. The cavity is elongated, and of the ten oxygens only eight at the same time can touch a potassium ion (in models). The cavity in models is elongated enough to accommodate two ions the size of potassium at the same time. Attempts to get higher than one-to-one complexation failed. The openings between strands of the _meso_ forms of 38 and 39 are much larger (in models) than those of the other isomers. No tests have yet been made with 39, or with the meso form of 38. No evidence is yet available as to whether potassium ion, which is much better bound than the others, actually enters the cage.

G. Syntheses of Two Multiheteromacrocycles with Two Negatively Polarized Oxygens Centered One Above and One Below the Hole (with Dr. Roger Helgeson)

From starting materials 40 and 42 (available from another study), cycles 41 and 43 were prepared in 80% yields. Molecular models of these compounds place the oxygens of the two P →O bonds directly above and below the centers of the holes of the cycles in what looks like almost perfect pentagonal bipyramidal and hexagonal bipyramidal arrangements of oxygen ligands.

40

41

42

43
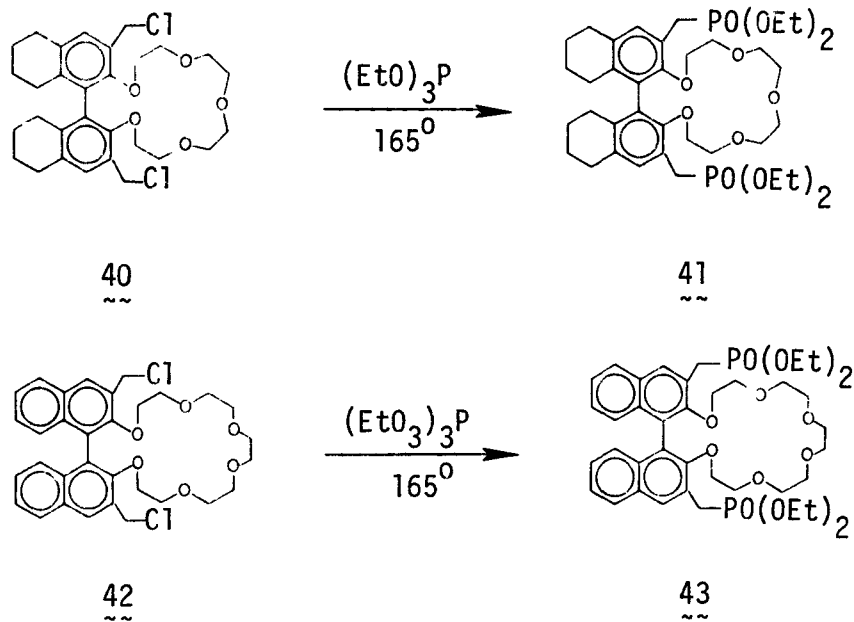
Although these compounds should be interesting in their own right as ion binders, the compounds with the phosphate esters hydrolyzed to the bis-phosphonic acids should be interesting potential scavengers for skeletal Pu^{4+} and U^{4+}. The compounds are being made specifically for testing by Dr. Walter Stevens of the University of Utah. The half-hydrolyzed esters should also be interesting compounds for complexing divalent ions.

Cooperation with Other ERDA Contractors

The principal investigator has had correspondence with Dr. R. R. Shoun of Oak Ridge Laboratory, and we sent a small amount of compound 44 for testing as a metal-complexing agent. We spent several mutually profitable days consulting at UCLA with Dr. B. E. Jepson of Mound Laboratories (particularly about Ca^{2+} and Li^{+} complexing agents), Dr. Walter Stevens of the University of Utah (about Pu^{4+} and U^{4+} complexing agents), and Dr. P. Gary Eller of Los Alamos Laboratory about the preferred ligand arrangements of certain metal ions
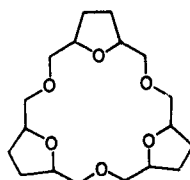
44

(particularly UO_2^{2+}) in crystal structures. We are pleased to send small samples of materials when they are available to other groups for testing. We are also very willing to make available our procedures for syntheses to other groups, so they can make or have made desired compounds in laboratories organized for that purpose.

Educational Profit from this Contract

A new field of organic host-inorganic guest chemistry is being developed under this contract. Three carefully chosen postdoctoral research chemists and the principal investigator are learning the science and art of multiheteromacrocycle synthesis, and enough inorganic chemistry to design our ligand assemblies. As time goes on, the same group will develop new test systems to determine the complexing properties of the systems synthesized. A whole new way of thinking about organic-inorganic chemistry is evolving, and it is our belief that we are cultivating a field that will attract many other research groups. Another twelve coworkers, who are primarily graduate students, are also learning this field by association with those who are creating this field. By the third year, graduate students are expected to join in this effort.

Publications

No publications have yet appeared based on work done under this contract, nor have any yet been submitted. Several will be submitted during 1976.