J. Am. Chem. Soc. 1980, 102, 5947-5948

that the peroxo-bridged dimer PFeOOFeP forms in the presence of potential axial ligands. Further studies of oxygenation transfer by iron porphyrin complexes are in progress.

Acknowledgments. We thank the National Institutes of Health (GM 26226) and the UCD NMR Facility for financial support, Alan Sargeson for stimulating discussions, and Katie Lindsay for dedicated experimental assistance.

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Received March 20, 1980

Macrocyclic Hexacarboxylic Acid. A Highly Selective Host for Uranyl Ion

Sir:

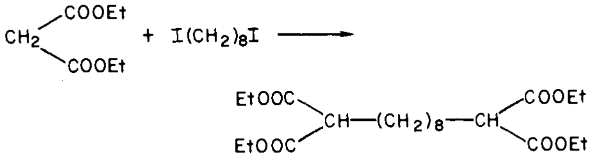
Macrocyclic polydentates have attracted enormous attention from chemists because of their unique and significant characterisitic of the strong and selective binding of a variety of metal ions.[1,2] The metal binding is governed mostly by the size of the macroring and the nature of heteroatoms involved. The most important role of the macrocyclic structure is, in general, the so-called "macrocyclic effect"[3] —to increase (making less negative) a large negative entropy change involved in the polydentate chelation.

Basic strategy then is to design a ligand of very strong metal binding to take advantage of this macrocyclic effect as well as the enthalpy effect (negative enthalpy change) associated with the chelation under consideration. For the latter purpose, a negatively charged ligand should be chosen as a strong candidate although only a few examples[4] are known in which anions are appropriately arranged in a macroring host.[5]

We have currently been interested in the highly selective binding of a family of metal ions of pseudoplanar hexacoordination,[6] to which uranyl (UO_2^{2+}) belongs as an important member from a practical viewpoint. As an application of the basic strategy described above to the solution of this rather difficult problem, we have prepared a macrocyclic hexaketone which bound uranyl ion effectively.[4e,7]

Now we report that selective members of the family, **3** and **4**, were newly designed. These ligands were prepared by symmetrically arranging six carboxylates on a macrocyclic skeleton in which the ring size was adjusted to give a cavity to accommodate uranyl ion comfortably. Three of the six carboxylates seem to compose a binding site. One of the three additional carboxylic acid units in either **3b** and **4** is amenable to attachment to a suitable polymer support. The other two probably act to make the microscopic environment around the metal binding site more hydrophilic as well as to decrease the entropy loss involved in the complexation. Compared with the previous hexaketone, the new macrocycle hexacarboxylic acids are capable of much more facile preparation in reasonable overall yields and are more effective and selective for the binding of the uranyl ion.

Preparation is straightforward and is described by eq 1-3.



(1)

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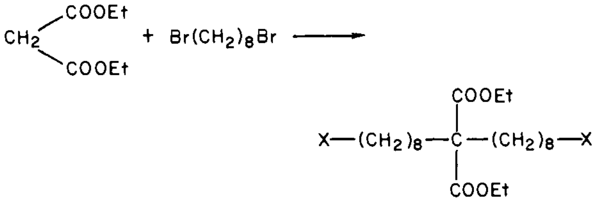
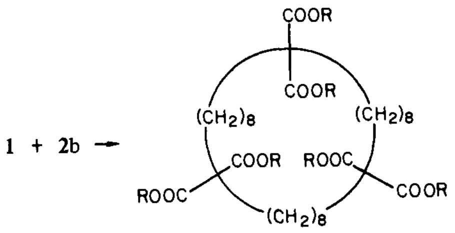


(2)

2a, X = Br
b, X = I



(3)

3a, R = Et
b, R = H

Tetraethyl n-decane-1,1,10,10-tetracarboxylate, **1**, and diethyl α,α-bis(8-iodooctyl)malonate, **2b**, were prepared according to the conventional method for the malonate synthesis and were obtained in 67% and 54% yields, respectively. The final cyclization was achieved under high-dilution conditions. For example, to a mixture of 1.7 g (3.9 mmol) of **1** and 2.5 g (3.9 mmol) of **2b** in 800 mL of THF was added 0.56 g (12 mmol) of sodium hydride dispersion (50%). After 20 h of refluxing followed by usual workup, the hexaethyl ester of macrocyclic hexacarboxylic acid, **3a**, was isolated through silica gel column chromotagraphy. The yield of colorless crystals obtained from n-hexane was 1.47 g (46%): mp 82–84 °C; IR (KBr) 1723 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (t, 18 H), 1.0–1.4 (br, 36 H), 1.4–2.0 (br, 12 H), 4.10 (q, 12 H); mass spectrum (hexamethyl ester), m/e 726 (M^+), 694 (base), 662, 634. Anal. Calcd: C, 66.64; H, 9.69. Found C, 66.63; H, 9.61. Alkaline hydrolysis of 1.52 g of **1a** yielded 1.11 g (92%) of hexacarboxylic acid **1b**: mp 200–205 °C; IR (KBr) 1697 cm^{-1}; NMR (Me_2SO-d_6) δ 1.0–1.5 (br, 36 H), 1.5–2.0 (br, 12 H), FD mass spectrum m/e 643 ($M^+ + 1$). Anal. Calcd: C, 61.66; H, 8.47. Found: C, 61.63; H, 8.49. Similar procedures gave a hexacarboxylic acid of type **4**, containing an ether bridge, in an overall yield of 17.5%. All of the spectral and analytical data are satisfactory.

Uranyl ion is known to form a stable complex with carbonate (CO_3^{2-}). The stability constant (log K_f) ranges from 20.7 to 23.0, depending on the conditions.[8] The addition of hexacarboxylic acid **3b** (1.0×10^{-3} M) to a uranyl tricarbonate solution (5.0×10^{-4} M in 1.0×10^{-2} M Na_2CO_3, pH 10.4) gave a change of visible

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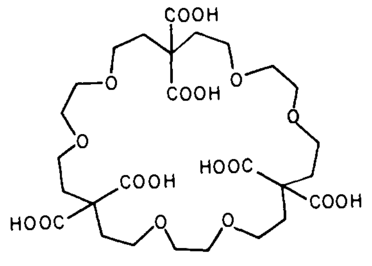

4

absorptions due to the competitive formation of the **3b**-UO_2^{2+} complex.[9] From this competitive binding, a relative formation constant, $K_{rel} = K_{3b-UO_2^{2+}}/K_{CO_3^{2-}-UO_2^{2+}}$, was estimated to be $10^{-5.1}$, giving a log $K_{3b-UO_2^{2+}}$ value of 16.4 at 25 °C. The value is the largest among the hosts ever reported to bind uranyl ion, an example of which is a macrocyclic β-diketone reported by Cram (log $K = 12.5$ in aqueous dioxane).[4c] The large stability constant observed for the present macrocyclic hosts seem to be due to appropriate ligand arrangement as well as to the strong ligation of carboxylate anion.

High selectivity of the present host to uranyl was ascertained also by competition with other metal cations. An ethereal solution of **3b** (4.2×10^{-4} M, 1 mL) was stirred with a dilute solution of uranyl acetate (3.2×10^{-5} M, 5 mL) in the presence of a large excess of a competing cation such as Na^+ (0.469 M), Mg^{2+} (7.82×10^{-2} M), pH 8, Ni^{2+} (1.70×10^{-4} M), or Zn^{2+} (3.06×10^{-4} M), pH 6. Selectivity factors $K_{M^{m+}}/K_{UO^{2+}}$ for these metal ions were determined from the decrease of uranyl complexation by competition, and their values are $Na^+ < 1/180000$, $Mg^{2+} < 1/31000$, $Ni^{2+} = 1/210$, and $Zn^{2+} = 1/80$.

These results portend the efficient extraction of the uranyl ion from sea water with the present hexacarboxylic acid ligand attached to a polymer completely insoluble in water. Thus, 100 mg of cross-linked polystyrene-bound hexacarboxylic acid **3b**[10] (capacity: 630 μg of uranium/100 mg of polymer) was stirred with 5 L of sea water (Pacific Ocean) for 4 days. The polymer beads were separated, and uranyl ion was liberated by treatment with 15% ammonium bicarbonate solution (10 × 6 mL). The amount of uranium liberated was determined to be 6.85 μg, which corresponds to 41.5% of the total uranium present in the sea water treated.

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(9) It is a slow rate process requiring several hours for equilibration, but too long of a reaction often caused precipitation.

(10) Styrene was copolymerized with 3 mol % of triethylene glycol dimethacrylate. The resulting copolymer was chloromethylated and reacted with N-(ω-hydroxyoctyl)phthalimide, followed by the hydrolysis of phthalimide. The amino function was reacted with the mixed anhydride of hexacarboxylic acid prepared from ethyl chloroformate and triethylamine.

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Received March 24, 1980

Selective Homogeneous Catalytic Hydrogenation of Polynuclear Aromatics

Sir:

In a preliminary report, we recently described the synthesis and characterization of $(Ph_3P)_2(Ph_2P\overline{C_6H_4)Ru}H_2^+K^+\cdot C_{10}H_8\cdot(Et_2O)$ (**1**). This anionic hydride complex was found to be particularly useful for the hydrogenation of organic compounds containing polarized multiple bonds, for example, ketones, esters, and nitriles.[1]

Table I. Hydrogenation of Polynuclear Aromatics[a]

catalyst	substrate	% conversion[b]	solvent
$(Ph_3P)_3RuHCl$	naphthalene	0	THF
1	naphthalene	67	THF
1	naphthalene	70	toluene
1 + 18-crown-6	naphthalene	65	toluene
1	2-methylnaphthalene	35	THF
1	anthracene	99	THF[c]
1	phenanthrene	2	THF

[a] Typical conditions: complex **1** (0.035 mmol); aromatic substrate (3.9 mmol); solvent (5 mL); hydrogen (620-kPa gauge); 100 °C; 20 h. [b] Conversions were determined by gas chromatography with a 2 m × 3.2 mm stainless-steel column containing 1.5% BMBT on Chromosorb WHP 100/120 mesh; 150 °C 1 min, 4 °C/min to 220 °C. Products were identified by GC/MS techniques, and by comparison with authentic samples. [c] This reaction was stopped after 2-h reaction time.

In the preparation of **1**, we found that it could be isolated as the naphthalene or toluene adducts. X-ray structural work presently in progress indicates that the naphthalene in **1** is present only as a molecule of crystallization. Because of the apparently high affinity of **1** for aromatic compounds, we decided to investigate it as a possible catalyst for the hydrogenation of arenes. It was found that tetrahydrofuran (THF) solutions of **1** catalyzed the hydrogenation of polynuclear aromatics, predominantly to their tetrahydro derivatives, at 100 °C and 620-kPa gauge of hydrogen. Thus, naphthalene was found to be hydrogenated exclusively to tetrahydronaphthalene. Anthracene was hydrogenated to tetrahydroanthracene (98% selectivity) and 1,2,3,4,5,6,7,8-octahydroanthracene (2% selectivity). Anthracene was hydrogenated at a much faster rate than naphthalene (see Table I). Phenanthrene, which was hydrogenated much more slowly than anthracene and naphthalene, gave tetrahydrophenanthrene (96% selectivity) and 9,10-dihydrophenanthrene (4% selectivity). 2-Methylnaphthalene was found to be hydrogenated predominantly to 5,6,7,8-tetrahydro-2-methylnaphthalene (89% selectivity) and 1,2,3,4-tetrahydro-2-methylnaphthalene (9% selectivity). As can be seen from Table I, the relative ease of hydrogenation of the polynuclear substrates by using complex **1** as the catalyst is as follows: anthracene ≫ naphthalene > 2-methylnaphthalene > phenanthrene.

Under the same conditions, isolated aromatic rings such as benzene, toluene, tetralin, and pyridine were not hydrogenated. The precursor to **1**, $(Ph_3P)_3RuHCl\cdot C_6H_5CH_3$, under the same conditions was found to be inactive for the hydrogenation of naphthalene.

Other transition-metal complexes have recently been shown to homogeneously catalyze the hydrogenation of arenes,[2-7] but only one other, $Co_2(CO)_8$, has been reported to selectively hydrogenate naphthalene to tetrahydronaphthalene.[7] Complex **1** offers an advantage over the cobalt catalyst since the latter requires 13 000-kPa gauge of carbon monoxide/hydrogen and 200 °C whereas **1** is active at 620-kPa gauge of hydrogen and 100 °C. Moreover, with anthracene, $Co_2(CO)_8$ yields exclusively 9,10-dihydroanthracene whereas **1** gives predominantly 1,2,3,4-tetrahydroanthracene. The soluble metal complex catalyst $[C_5(CH_3)_5RhCl_2]_2$ in the presence of triethylamine has been reported to hydrogenate anthracene to tetrahydroanthracene (70%) and octahydroanthracene (22%).[4] Its reactivity with naphthalene,

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