$[PPN][MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]$, and an ORTEP diagram of the anion (11 pages); a listing of structure factors (40 pages). Ordering information is given on any current masthead page.

Department of Chemistry
Northwestern University
Evanston, Illinois 60208-3113

Eric J. Voss
Michal Sabat
Duward F. Shriver*

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New Synthetic Route to the Hydridospherosiloxanes O_h-$H_8Si_8O_{12}$ and D_{5h}-$H_{10}Si_{10}O_{15}$

Oligomeric silsesquioxanes are compounds of general formula $(XSiO_{1.5})_n$ where n is an even number ($n \geq 4$) and X is either H, Cl, or any of a large number of organic groups.[2-5] The name "spherosiloxanes" is sometimes used to describe these compounds,[6,7] since they have polyhedral structures that are topologically equivalent to a sphere.

The first hydridospherosiloxane was synthesized serendipitously in 1959 by Müller, Köhne, and Sliwinski[8] (<1% yield from $HSiCl_3$) and shown to be O_h-$H_8Si_8O_{12}$. Subsequently, in 1970 an improved synthesis of this compound was reported by Frye and Collins[3] (ca. 13% yield from $HSi(OCH_3)_3$). They also reported an unusual preparative procedure that yielded a mixture of hydridospherosiloxanes in highly variable yields (15–35% from $HSiCl_3$). Agaskar, Day, and Klemperer reported in 1987[9] that a modification of this procedure gave more reproducible yields (>30%) and also described a purification protocol that yielded gram quantities of four pure hydridospherosiloxanes. The structures of these compounds O_h-$H_8Si_8O_{12}$, D_{5h}-$H_{10}Si_{10}O_{15}$, D_{2d}-$H_{12}Si_{12}O_{18}$, and D_{3h}-$H_{14}Si_{14}O_{21}$, which were obtained in ca. 0.5, 3.5, 3.5, and 0.5% yields, respectively, are shown in Figure 1.

We wish to report here that we have now developed a new synthetic procedure that is extremely easy to implement and that gives a mixture of O_h-$H_8Si_8O_{12}$ and D_{5h}-$H_{10}Si_{10}O_{15}$ (ca. 3.5:1) in ca. 27.2% yield. Pure O_h-$H_8Si_8O_{12}$ can be isolated from the mixture of crystals in ca. 17.5% yield as described below, while pure D_{5h}-$H_{10}Si_{10}O_{15}$ can be isolated from the remainder by following procedures published earlier.[10]

The fundamental feature of this procedure is the use of a partially hydrated metal salt solution to create "scarce-water" hydrolysis conditions similar to those involved in the preparation that uses sulfuric acid.[3,9]

The hydridospherosiloxanes are potentially a very useful class of compounds[11-14] whose chemistry has remained underdeveloped because of the lack of a facile method of making them in synthetically useful quantities. The experimental procedure that is described below should make at least two of these widely accessible, while modifications of this procedure could lead to efficient and convenient synthesis of other compounds of this type.

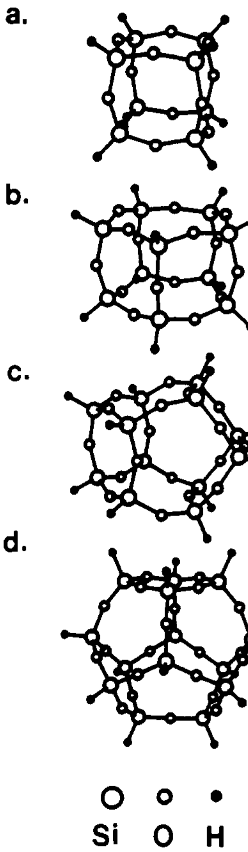

Figure 1. Structures of the four pure hydridospherosiloxanes that have been prepared in gram quantities: (a) O_h-$H_8Si_8O_{12}$; (b) D_{5h}-$H_{10}Si_{10}O_{15}$; (c) D_{2d}-$H_{12}Si_{12}O_{18}$; (d) D_{3h}-$H_{14}Si_{14}O_{21}$.

Experimental Procedure. $FeCl_3$ (anhydrous, 50 g) was taken in a round-bottomed flask, and concentrated HCl (20 mL) was added followed by CH_3OH (40 mL). C_6H_{14} (mixture of isomers, 350 mL) and C_7H_8 (50 mL) were then added, and the biphasic mixture was stirred by a heavy magnetic stirrer. A solution of $HSiCl_3$ (20 mL, ~0.2 mol) in C_6H_{14} (150 mL) was added dropwise by using a pressure-equalizing dropping funnel over a period of 9 h. After an additional 30 min of stirring, the upper hexane layer was transferred to another round-bottomed flask along with some suspended yellow solid (the $FeCl_3$-containing layer can be reused after addition of concentrated HCl).[15] K_2CO_3 (14 g) and $CaCl_2$ (10 g) were added to the flask and the contents stirred overnight. The mixture was filtered, and the filtrate volume was reduced by evaporation until it was ca. 20 mL. The crystals that were deposited weighed 1.86 g after they were separated from the mother liquor and washed with some hexane. The washings were combined with the mother liquor, and the volume was reduced further by evaporation until it was <10 mL. A second crop of crystals was collected (1.02 g) and washed with hexane. The total yield of white crystals was 2.88 g. The mother liquor contained 4.9 g of a soluble product.

^1H NMR spectroscopy (C_6D_6, 270 MHz) showed that these crystals were a mixture (ca. 3.5:1) of O_h-$H_8Si_8O_{12}$ (δ = 4.203 ppm)[9] and D_{5h}-$H_{10}Si_{10}O_{15}$ (δ = 4.244 ppm).[9] The total yield based on $HSiCl_3$ was 27.2%.

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(1) Current address: Central Research Laboratory, Mobil Research and Development Corp., P.O. Box 1025, Princeton, NJ 08540.
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(15) The procedure was repeated by using this recycled $FeCl_3$ layer and a drop-in time of only 4.5 h to give O_h-$H_8Si_8O_{12}$ in 16.8% yield based on $HSiCl_3$.

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When this mixture was washed with hexane (ca. 45 mL), all the D_{5h}-$H_{10}Si_{10}O_{15}$ was removed along with some O_h-$H_8Si_8O_{12}$. The residue was pure O_h-$H_8Si_8O_{12}$ (1.85 g; yield based on $HSiCl_3$ 17.5%).[16]

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Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Pradyot A. Agaskar[1]

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[16] Since the crystals were obtained from a filtered solution and were observed to dissolve completely in C_6D_6, it was assumed that they were not contaminated with SiO_2. The ^{29}Si satellites ($^1J_{Si-H}$ = ~170 Hz) were used to rule out any significant contamination by other $(HSiO_{1.5})_n$ species.

Articles

Contribution from the Dipartimento Scienze Chimiche, Università di Catania, 95125 Catania, Italy, and Istituto per lo Studio delle Sostanze Naturali di Interesse Alimentare e Chimico-Farmaceutico, CNR, 95125 Catania, Italy

Conformational Features and Coordination Properties of Functionalized Cyclodextrins. Formation, Stability, and Structure of Proton and Copper(II) Complexes of Histamine-Bearing β-Cyclodextrin in Aqueous Solution

Raffaele P. Bonomo,[1a] Vincenzo Cucinotta,[1a] Franca D'Alessandro,[1a] Giuseppe Impellizzeri,[1a] Giuseppe Maccarrone,[1a] Graziella Vecchio,[1b] and Enrico Rizzarelli*[,1a,b]

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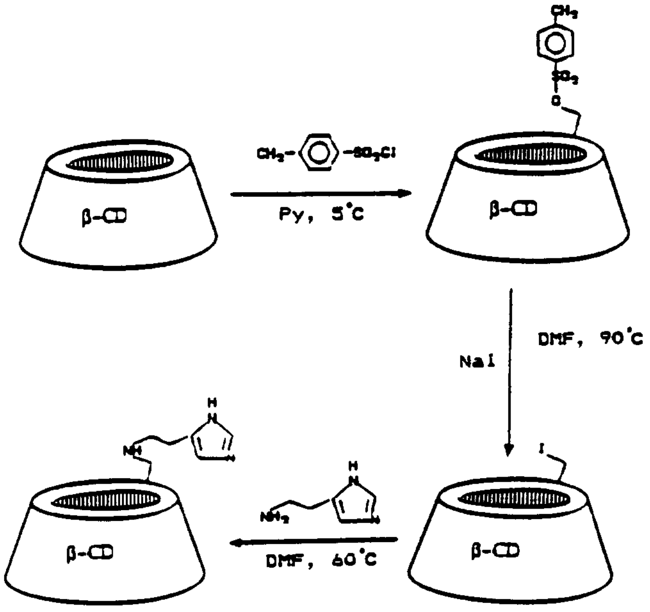
The functionalized cyclodextrin 6-deoxy-6-(*N*-histamino)-β-cyclodextrin was synthesized, and an NMR, EPR, pH-metric, and calorimetric investigation was carried out in aqueous solution in order to ascertain its behavior toward protonation and copper(II) complexation. Spectroscopic results as well as thermodynamic data give evidence of the influence of the β-cyclodextrin cavity. In particular, the NMR spectra data show a protonation-promoted inclusion of the imidazole ring, while the copper(II) coordination is markedly affected by the presence of the cyclodextrin cavity, as shown by the $A_\parallel$ value decrease, with respect to the analogous histamine complex.

Introduction

Cyclodextrins have been proposed as artificial enzymes due to their ability to form inclusion compounds and to show regiospecificity and stereospecificity with respect to the substrate and to the product during catalytic processing.[2-6] The introduction of functional groups has provided more efficient models of natural enzymes and receptors.[7-13] Furthermore, for more sophisticated molecular recognition, double (or multiple) recognition systems have been obtained by means of the metal complexes of functionalized cyclodextrins where the additivity of cavity and metal-ligand interaction has been demonstrated.[14-18]

Scheme I



Inclusion compounds have also been reported for the metal complexes of cobalt(III), iron(0), rhodium(I), ruthenium(0), and platinum(II), in which cyclodextrins behave like second-sphere ligands.[19-25]

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(1) (a) Università di Catania. (b) Istituto per lo Studio delle Sostanze Naturali di Interesse Alimentare e Chimico Farmaceutico, CNR.
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