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Tunable Supramolecular Structures from a Gluconamide Containing Imidazole

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In recent years, the interest in supramolecular structures has grown steadily. Self-assembling systems have been prepared from a variety of building blocks including surfactants,[1] polymers,[2] rod-like[3] and disk-like mesogens[4] etc. As part of our program aimed at the development of novel chiral matrices for catalytic applications, we report here on the synthesis and self-assembling properties of the n-octyl-l-gluconamide derivative 3, which contains a metal-coordinating imidazole group. Our interest in gluconamides and related carboxylates was raised by the recent studies of Fuhrhop et al. and others,[5] which indicate that these compounds can form a great variety of nanometer-sized structures in water.

Compound 3 was synthesized as shown in Scheme 1. 1,5-D-Gluconolactone was hydrolyzed and protected at its secondary hydroxyl functions in a one-step procedure.[7] The resulting product was esterified to give methyl-2,4,3,5-dimethylene-D-glucosiate which was amidonized with octylamine to give the amide 2. The latter compound was tosylated and subsequently converted into 3 by reaction with imidazole in an autoclave at high pressure (15 Kbar).

Although the polarity of carbohydrate 2 is decreased due to the methylene bridges, it appears that this compound is soluble in water. However, unlike the unprotected derivative, it does not form well-defined aggregates, as judged by electron microscopy (EM). Apparently, the amide bond and the primary hydroxyl function in 2 cannot form hydrogen bonds leading to stable suprastructures in water. The DSC studies (DSC = differential scanning calorimetry) of an aqueous solution of 2 showed only one transition near 43 °C, which can be assigned to the disappearance of amide hydrogen bonds. No transition was observed upon cooling.[8] The thermogram of n-octyl-D-gluconamide shows two transitions upon heating,[9] which are attributed to the breaking of a network of intermolecular hydrogen bonds between the hydroxyl groups (at 61 °C), and between the amide hydrogen bonds (at 70 °C).[10] Compound 3 is also soluble in water. From a titration experiment in methanol/water (95/5, v/v), it followed that the apparent pKₐ value (pKₐ) of the imidazole group is 6.28. For comparison, methylimidazole and imidazole were also titrated in this solvent.[11] From these data, the secondary amide hydrogen bonds (at 70 °C), and between the amide hydrogen bonds (at 70 °C).[12] The copper complexation properties of 3 were investigated by UV/VIS controlled titrations. Addition of Cu(CIO₄)₂ to a solution of 3 in water led to the appearance of a broad band at approximately λ = 620 nm. Unfortunately, the complex [Cu(3)]⁺ was not soluble enough in water to carry out an accurate UV/VIS titration. In mixtures of organic solvents such as chloroform/methanol (1/2, v/v), clear solutions were obtained and the complexation behavior of 3 could be determined. No transition was observed upon cooling.[8] The thermogram of n-octyl-D-gluconamide shows two transitions upon heating,[9] which are attributed to the breaking of a network of intermolecular hydrogen bonds between the hydroxyl groups (at 61 °C), and between the amide hydrogen bonds (at 70 °C).[10] Compound 3 is also soluble in water. From a titration experiment in methanol/water (95/5, v/v), it followed that the apparent pKₐ value (pKₐ) of the imidazole group is 6.28. For comparison, methylimidazole and imidazole were also titrated in this solvent.[11] From these data, the secondary amide hydrogen bonds (at 70 °C), and between the amide hydrogen bonds (at 70 °C).[12] The copper complexation properties of 3 were investigated by UV/VIS controlled titrations. Addition of Cu(CIO₄)₂ to a solution of 3 in water led to the appearance of a broad band at approximately λ = 620 nm. Unfortunately, the complex [Cu(3)]⁺ was not soluble enough in water to carry out an accurate UV/VIS titration. In mixtures of organic solvents such as chloroform/methanol (1/2, v/v), clear solutions were obtained and the complexation behavior of 3 could be determined. During the titrations of 3 with Cu(CIO₄)₂, the λₘₐₓ gradually shifted from 600 to 780 nm when the ratio [Cu]/[3] was increased.
from 1/4 to 1/1. The titrations revealed that at low copper concentrations a 4/1 ligand-to-copper complex\(^{[12]}\) is present, whereas at high copper concentrations other complexes, for example \([3]/[Cu] = 3, 2, \text{ or } 1\) prevail. For comparison, titrations were also carried out with the non-ampiphilic imidazole compound \(4^{[13]}\) and with methylimidazole. In both water and methanol/chloroform mixtures the copper complexation curves of \(3, 4, \text{ and } N\)-methylimidazole were very similar.

The types of aggregates formed by \(3\) in water were studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). In a NaOAc/HOAc buffer of pH 4.5, protonated \(3\) self-assembles to yield vesicles (100%) with diameters ranging from 160 to 780 nm (Fig. 1A).\(^{[14]}\) In a tris(hydroxymethyl)aminomethane (TRIS) buffered solution of pH 8.5 this solution was placed on a hydrophilic formvar supported grid. The vesicles can have a length/width ratio up to 500 (Fig. 1B, the diameters of these fibers are approximately 100 nm). Freeze fracture techniques showed that these fibers are composed of multilayers (not shown). The hollow tubuli have diameters of approximately 3 \(\mu\)m in a TRIS buffered solution, (pH 8.5), the 1:4 copper complex of amphiphile \(3\) forms helices (100%, diameter approximately 3 \(\mu\)m). In a TRIS buffered solution of pH 8.5 long fibers (Fig. 1B and C) can be tuned by changing the pH or by adding metal ions. Freeze fracture of these fibers are approximately 100 nm. Freeze fracture techniques showed that these fibers are composed of multilayers (not shown). The hollow tubuli have diameters of approximately 3 \(\mu\)m in a TRIS buffered solution, (pH 8.5), the 1:4 copper complex of amphiphile \(3\) forms helices (100%, diameter approximately 3 \(\mu\)m). In a TRIS buffered solution of pH 8.5 long fibers (Fig. 1B and C) can be tuned by changing the pH or by adding metal ions.

In conclusion, we have shown that gluconamide can self assemble to give interesting supramolecular structures which can be tuned by changing the pH or by adding metal ions.

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\[\text{COMMUNICATIONS} \]

Iodine Chains in \((Me_4Sb)_2I_3\) and Discrete Triiodide Ions in \(Me_4AsI_3\)**

Ulrich Behrens, Hans Joachim Breunig,* Michael Denker, and Klaus Heinz Ebert

Polyyiodides have an extensive structural chemistry,\(^{[1]}\) and compounds with discrete iodine chains are of particular interest because of possible unusual electric behavior.\(^{[2]}\) Iodine and iodide chains are not rare. They occur, for example, in the iodine-starch complex and in related compounds,\(^{[3]}\) in organic metals,\(^{[4]}\) in complexes with column structures,\(^{[5]}\) and also in saltlike triiodides such as \(Bu_NI_2\).\(^{[6]}\) The iodine chains in these compounds frequently consist of triiodide or iodide ions and iodine molecules.\(^{[7]}\) Ordered iodine chains such as in \((CdNH_3)_2I_4\) are unusual;\(^{[8]}\) in this complex the iodine chains are not discrete, but are linked three-dimensionally by strong coordinative bonds to

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