COMMUNICATIONS

...dinium ion, the long-wavelength band disappears. Our long-term goal with these investigations is to be able toenantioselec-
tively control not only the spectroscopic behavior but also the reactivity of prochiral guest molecules.

Received: November 29, 1993 [Z5521IE]
German version: Angew. Chem. 1994, 106, 1041


...sponding. Addition of Cu(C104)2 to a
...of 3 in water led to the appearance of a broad band
...llows that the appearance of a broad band
...tive. 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,[10,11] 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).[9]

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.[11] For comparison, methylimidazole and imidazole were also titrated in this 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).[9]

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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-amphiphilic imidazolide compound \(4\)\(^{[13]}\) and with methylimidazole. In both water and methanol/chloroform mixtures the copper complexation curves of 3, 4, 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)methyamine (TRIS) buffered solution of pH 8.5 long fibers (Fig. 1B and C) and hollow tubuli are formed exclusively (Fig. 1C). The fibers can have a length/width ratio up to 500 (Fig. 1B, the diameters of these fibers are approximately 100 nm).\(^{[15]}\) Freeze fracture experiments showed that these fibers are composed of multilayers (not shown). The hollow tubuli have diameters of approximately 3 μm. In a TRIS buffered solution, (pH 8.5), the 1:4 copper complex of amphiile 3 forms helices (Fig. 1D).\(^{[16]}\) The diameters of these helices are approximately 330 nm; much larger than the ropelike structures formed by \(N\)-octyl-D-gluconamide (diameter of 27 nm).\(^{[17]}\)

In conclusion, we have shown that gluconamide 3 can self-assemble to give interesting supramolecular structures which can be tuned by changing the pH or by adding metal ions.

Iodine Chains in (Me4Sb)3I8 and Discrete Triiodide Ions in Me4AsI3**
Ulrich Behrens, Hans Joachim Breunig,* Michael Denker, and Klaus Heinz Ebert

Polyiodides have an extensive structural chemistry,\(^{[18]}\) and compounds with discrete iodine chains are of particular interest because of possible unusual electric behavior.\(^{[19]}\) Iodine and iodide chains are not rare. They occur, for example, in the iodine–starch complex and in related compounds,\(^{[20]}\) in organic metals,\(^{[21]}\) in complexes with column structures,\(^{[22]}\) and also in saltlike triiodide chains that are linked three-dimensionally by strong coordinative bonds to iodine and iodide ions.\(^{[23]}\)

** This work was supported by the Fonds der Chemischen Industrie. We thank Mrs. L. Akrouch and Dr. S. Roth, Max-Planck-Institut für Festkörperforschung, Stuttgart, for the conductivity measurements, Prof. Dr. O. Jarchow, Mineralogisch-Petrographisches Institut der Universität Hamburg, for the discussion of the X-ray crystallography investigations.