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

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[8] For an example of a diastereoselective ring closure reaction of a biaryl derivative leading to kinetic separation of isomers, see: G. Brüngmann, J. R. Jansen, H. Busse, Liebigs Ann. Chem. 1991, 803–812; see also [2e,f].


Tunable Supramolecular Structures from a Glucamidone Containing Imidazole

Rudi J. H. Haakamp, Martinus C. Feiters,* and Roeland J. M. Nolte*

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,[14] polymers,[15] rodlike,[16] and disklike mesogens[4,5] 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-$\alpha$-glucamidone derivative 3, which contains a metal-coordinating imidazole group. Our interest in glucamidones and related carbohydrates was raised by the recent studies of Fuhrhop et al. and others,[10] 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-Glucolanolactone 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;3,6-dideoxy-$\alpha$-L-gluconate which was aminolyzed 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,[8,10] 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-$\alpha$-glucamidone shows two transitions upon heating,[8] 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 pK$\alpha$ value (pK$\alpha$) of the imidazole group is 6.28.[10] For comparison, methylimidazole and imidazole were also titrated in this stable suprastructure 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-$\alpha$-glucamidone shows two transitions upon heating,[8] 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]

The copper complexation properties of 3 were investigated by UV/VIS controlled titrations. Addition of Cu(ClO$_4$)$_2$ to a solution of 3 in water led to the appearance of a broad band at approximately $\lambda = 620$ nm. Unfortunately, the complex [Cu(3)]$^{2+}$ 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(ClO$_4$)$_2$, the $\lambda_{max}$ 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 \([3]/[Cu] = 3, 2,\) or 1 prevail. For comparison, titrations were also carried out with the non-amphiphilic imidazole compound \(4^{[13]}\) and with methylimidazole. In both water and methanol/chloroform mixtures the copper complexation curves of 3, 4, and \(N\)-methyllumidazole 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 give interesting supramolecular structures which can be tuned by changing the pH or by adding metal ions.

In conclusion, we have shown that gluconamide 3 can self-assemble to give interesting supramolecular structures which are linked three-dimensionally by strong coordinative bonds to form \(N\)-octyl-\(d\)-gluconamide (diameter of 27 nm).\(^{[60]}\)

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Iodine Chains in \((Me_4Sb)_3I_x\) and Discrete Triiodide Ions in \(Me_4AsI_3^{**}\)

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

Polyiodides have an extensive structural chemistry,\(^{[11]}\) 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,\(^{[12]}\) in organic metals,\(^{[2]}\) in complexes with column structures,\(^{[13]}\) and also in saltlike triiodides such as \(Bu_4NI_3.\)\(^{[14]}\) The iodine chains in these compounds consist of triiodide or iodide ions and iodine molecules.\(^{[15]}\) Ordered iodine chains such as in \([Cd(NH_3)_4I_6\] are unusual;\(^{[16]}\) in this complex the iodine chains are not discrete, but are linked three-dimensionally by strong coordinative bonds to

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[8] DSC analyses were carried out on a Perkin Elmer DSC 7 using a 4.9% (w/v) aqueous dispersion in a sealed pan, heating and cooling down rate was 5 Kmin⁻¹.


[10] The titration was carried out under a nitrogen atmosphere and the electrode was calibrated with a sodium succinate/succinic acid and an ammonium oxalate/oxalic acid buffer. D. Perrin, B. Dempsey, Buffers for pH and Metal Ion Control, Wiley, London, 1974.


[14] Aqueous samples for EM were prepared by cooling a hot clear solution of 3 in NaOAc/HOAc buffer of pH 4.5 to room temperature. Subsequently, a drop of this solution was placed on a hydrophilic Formvar supported grid. The vesicles were stained with uranyl acetate (2%).

[15] For the electron micrographs a hydrophilic Formvar supported grid was used.

[16] To a hot clear solution of 3 (0.5% m/v) in TRIS buffer, 0.25 equiv of CuCl₂ was added. The turbid mixture was cooled rapidly to room temperature and allowed to stand for 30 min. No additional staining was used.

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